

NITROACETYLENES

**SYNTHESIS AND REACTIONS OF A NEW CLASS
OF COMPOUNDS**

von

Volker Jäger

aus

Nürnberg

1970 № 432



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SYNTHESIS AND REACTIONS OF A NEW CLASS OF COMPOUNDS

Der Naturwissenschaftlichen Fakultät

der Friedrich-Alexander-Universität Erlangen-Nürnberg

zur

Erlangung des Doktorgrades

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von

Volker Jäger

aus

Nürnberg

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3. Berichterstatter :	Professor Dr. H.J. Bestmann

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Topic and Scope of this Work.

The aim of this work was to synthesize nitroacetylenes, and if this should turn out successful, to study the reactions of this new class of compounds. Nitroacetylenes had already been described in the literature, but from the state of knowledge in organic chemistry already before this work these reports seemed doubtful and, in fact, were proven hereby to be wrong.

The problem "nitroacetylenes" had arisen from studies on hetero-substituted olefins and acetylenes carried out by H.G. Viehe and coworkers formerly in the laboratories of Union Carbide European Research Associates in Brussels and now at the University of Louvain. The attempts at nitroacetylene synthesis had been prepared by my Diploma Thesis on "A Novel Rearrangement of Substituted Propenes: The Equilibrium of the Four Isomeric Nitropropenes", directed by Prof. G. Hesse at the University of Erlangen-Nürnberg.

In nitroacetylenes, the triple bond is polarized in the opposite sense to that in the reactive ynamines. Because of the strongly electro-negative nitro group, nitroacetylenes promised to be highly reactive as well, but contrary to the former as electrophiles, and also as dipolarophiles and dienophiles. Nitroacetylenes, however, should also be of such a high ground state energy that one would expect the thermal stability of these compounds to be limited. Hopefully stabilization should be introduced into the nitroacetylenic system either by electronic or steric means. The first nitroacetylene

synthesis^[1] was achieved according to the latter principle and therefore we concentrated on this route. Starting compounds were 2-halo-1-nitroolefins because halo-nitroolefins with halogen in the 1-position had failed to give the desired nitroacetylenes by HX elimination as has been stated by other groups likewise.

From 1-halo-, i.e. 1-bromo-1-nitroolefins, Loevenich and coll. in 1930 thought to have isolated nitroacetylenes by the HX elimination of primary and secondary amines^[2]. In fact, in the course of this work these results were shown to be erroneous^[1], and another statement of Novikov and coll. from 1960, concerning a presumed p-nitrophenylnitroacetylene^[3], had to be revised similarly. The structure elucidation of the above compound caused a time-consuming deviation into the chemistry of heterocycles until the problem was resolved in a satisfactory manner^[4].

In the meantime, tert-butyl nitroacetylene was obtained via the easily accessible 2-iodo-1-nitroolefins in almost quantitative yield^[1]. The physical and chemical properties of this first authentic representative of its class once more confirmed our negative results in the reinvestigations mentioned above. The relatively high stability of

[1] V. Jäger and H.G. Viehe, *Angew. Chem.* 81, 259 (1969); *ibid. internat. Edit.* 8, 273 (1969).

[2] a) J. Loevenich, J. Koch, and U. Pucknat, *Chem. Ber.* 63, 636 (1930);
b) J. Loevenich and H. Gerber, *ibid.* 63, 1707 (1930).

[3] S.S. Novikov, V.M. Belikov, V.F. Dem'yanenko, and L.V. Lapshina, *Izvest. Akad. Nauk SSSR, Otdel. Chim.* 1960, 1295; *C.A.* 55, 423d (1961).

[4] H.G. Viehe, V. Jäger and F. Compennolle, *Angew. Chem.* 81, 999 (1969); *ibid. internat. Edit.* 8, 979 (1969).

the tert-butyl derivative — the iso-propyl and n-propyl nitroacetylenes decompose much more readily — made it a useful model compound to study the reactions of the nitroacetylene system^[5]. The high reactivity even of this sterically unfavoured tert-butyl derivative permitted a series of facile addition and cycloaddition reactions, in which the nitro group remained unchanged. Of course, only a small part of the known reactions of triple bond systems and especially of nitro-olefins could be carried out due to the limited time of this work. One reaction — that of tert-butyl nitroacetylene with ynamines — was studied in some detail, because of the theoretical and preparative interest in the potential cyclobutadiene formation. However, in this case, the nitro group no longer behaved as an inert substituent but reacted to unexpected rearranged products^[6].

[5] Presented in part at the GdCh meeting, Hamburg, Sept. 1969; and at the BASF, Ludwigshafen, April 1970.

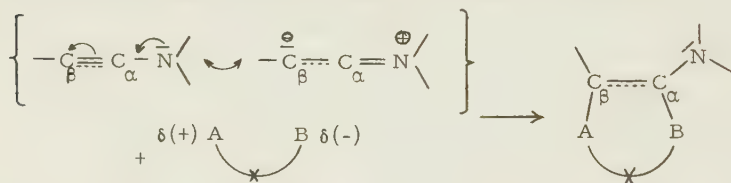
[6] a) V. Jäger and H.G. Viehe, Angew. Chem., in press.

b) H.G. Viehe and V. Jäger, Tetrahedron, in preparation.

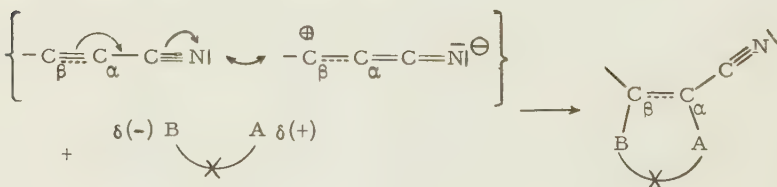
DISCUSSION

Introduction.

Hydrocarbon multiple bonds become particularly reactive when polarizing substituents are introduced. An example of a strong heteroatomic donor substituent is the dialkylamino group which renders α, β -unsaturated systems reactive: the chemistry of enamines^[7] and ynamines^[8] is characterized by the nucleophilic properties of their multiple bonds. Due to the polarization, addition reactions always proceed according to this scheme:



A nitrile or an ester group as substituents also increase the reactivity of adjacent multiple bonds. However, the orientation of the added molecule is different:



[7] For a review see A.G. Cook (ed.), "Enamines: Synthesis, Structure and Reactions", M. Dekker Inc., New York-London 1969.

[8] Reviewed by H.G. Viehe:

a) Angew. Chem. 79, 744 (1967); *ibid.* internat. Edit. 6, 767 (1967)

b) Chapter 12 (Ynamines) in H.G. Viehe (ed.), "Chemistry of Acetylenes"; M. Dekker Inc., New York-London 1969.

A common factor of both substituents, amino and nitrile group, is that the activation of α, β -unsaturated systems is mostly due to mesomeric effects, though in both cases there is also an electron-withdrawing inductive effect:



This -I effect is very marked in fluoro and ammonium compounds. For example, in fluoroolefins and fluoroacetylenes^[9] this leads to high reactivity and thermal instability. Of course, in simple acetylenes, addition reactions of the triple bond with other reagents or even with itself are thermodynamically favoured^[10]; the acetylenic bond is weaker, relatively, than the double bond formed. In other words, the high ground state energy in fluoroacetylenes deriving from the combination of quite electronegative sp carbon^[11] with the most electronegative element, is the driving force that the whole system tends to stabilize on changing to less electronegative sp^2 and further sp^3 carbon atoms.

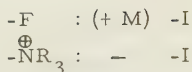
In principle, enammonium^[12] and the scarcely known ynammonium^[8] compounds are expected to show a similar behaviour though the slight +M effect found in fluoroacetylenes is not possible here:

[9] Review by S. Delavarenne and H.G. Viehe in loc. cit. [8b], Chapter 10 (1-Halogenoacetylenes).

[10] J. Dale in loc. cit. [8b], Chapter 1 (Structure and Physical Properties of Acetylenic Compounds; The Nature of the Triple Bond).

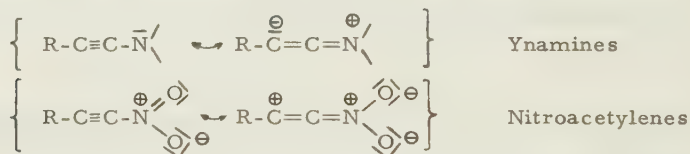
[11] sp^3 -C 2.5, sp^2 -C 2.8, sp -C 3.1 on the electronegativity scale; cp. A.D. Walsh, Disc. Far. Soc. 2, 18 (1947) and W. Gordy, J. Chem. Physics 14, 305 (1946).

[12] P.A.S. Smith, "Open-Chain Nitrogen Compounds"; Vol. 2, W.A. Benjamin, Inc., New York-Amsterdam 1966, p. 78.



As pointed out above, substituents with strong inductive and/or mesomeric effects at multiple bonds give rise to highly reactive classes of compounds. Many examples for this have been studied by H.G. Viehe and his group working mostly on the syntheses and reactions of heterosubstituted olefins and acetylenes^[13]; tert-butyl fluoroacetylene and its surprising oligomerisation to valence isomers of benzene^[14] and ynamines, a class of for the most part stable and very versatile reagents^[8] shall be mentioned to illustrate this.

The number of useful ynamine reactions and the expected reverse polarization of the conjugated π electron system in nitroacetylenes challenged to start investigations in this field.



From the above formulas one can see that the orientation of addition reactions to the nitroacetylene triple bond corresponds to what has been discussed for cyanoacetylenes. The nitro group exerts inductive and mesomeric effects both of high magnitude and polarizing an α, β -unsaturated system in the same direction. Its strong inductive effect is reflected clearly when the acidities of substituted acetic acids are compared:

[13] Heterosubstituted Acetylenes, Part 30, S. Y. Delavarenne and H. G. Viehe, Chem. Ber. 103, 1216 (1970).

[14] Review: H. G. Viehe, Angew. Chem. 77, 768 (1965); *ibid.* internat. Edit. 4, 746 (1965).

pK_a of $X-CH_2-COOH$ ^[15]:

X	NO ₂	Me ₃ N [⊕]	CN	F	Cl	COOEt	H
pK_a	1.68	1.83	2.43	2.66	2.86	3.35	4.76

Similarly, the pmr chemical shifts of CH_3-X compounds are related to the electronegativity of the substituent X, though in some cases (CN, CHO) strong anisotropic effects interfere:

Chemical shifts of CH_3-X (TMS: $\delta = 0$ ppm);
solvent CCl_4 , extrapol. to infinite dilution^[16].

X	NO ₂	F	Cl	Me ₃ N [⊕]	CN	H
δ	4.72	4.67	3.46	3.33*	2.32	0.13**

* in CF_3COOH ; ** gas

Laszlo and Schleyer in 1963 calculated electronegativity values for organic functional groups from the chemical shifts and coupling constants in 5-endo-substituted norbornenes^[17]. For the nitro group a value of 3.70 was found^[17]. This once again confirms the strong inductive effect of the nitro group almost equalling that of fluorine.

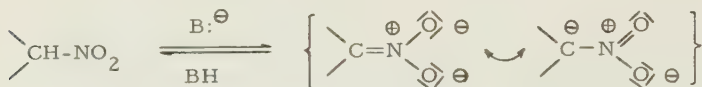
[15] a) E.S. Gould, "Mechanismus und Struktur in der organischen Chemie", Verlag Chemie GmbH, Weinheim 1964, p. 242.

b) P. Sykes, "A Guide to Mechanism in Organic Chemistry", Longmans, London 1967, p. 44.

[16] H. Suhr, "Anwendungen der kernmagnetischen Resonanz in der organischen Chemie", Springer-Verlag, Berlin-Heidelberg-New York 1965, pp. 93, 110, 118.

[17] P. Laszlo and P. von R. Schleyer, J. Amer. chem. Soc. 85, 2709 (1963); cf. also D.H. McDaniel and A. Yingst, *ibid.* 86, 1334 (1964).

Both inductive and mesomeric effects of the nitro group are responsible for the unique acidity of nitroalkanes, where the conjugated anions are stable even in aqueous solutions^[18]:



As shown in equilibrium measurements of α, β - and β, γ -unsaturated nitroolefins, in these systems normally conjugation is preferred^[19]. For example, at 20° the free standard reaction enthalpy ΔG is 3.5-4.0 kcal for the equilibrium 3-nitro-1-propene $\rightleftharpoons$ trans-1-nitro-1-propene^[19a, e].



Thus in nitro compounds both effects are important:



[18] P.A.S. Smith, "Open-chain Nitrogen Compounds", Vol. 2, W.A. Benjamin, Inc., New York-Amsterdam 1966, p. 394f.

[19] a) V. Jäger, Diploma Thesis, Univ. Erlangen-Nürnberg 1969 and references therein ; compare also
 b) G. Hesse, R. Hatz and H. König, Liebigs Ann. Chem. 709, 79 (1967).
 c) P. Schagerl, Diploma Thesis, Univ. Erlangen-Nürnberg 1968.
 d) P. Werkhoff, Diploma Thesis, Univ. Erlangen-Nürnberg 1969.
 e) G. Hesse and V. Jäger, Liebigs Ann. Chem., in press.
 f) G. Hesse, V. Jäger and P. Schagerl, *ibid.*, in preparation.

[20] loc. cit. [12], Chapter 14.

The electronegativities of the nitro group and of fluorine are comparable, hence the stability of the nitroacetylene system, too, should be quite limited. As known from the lower members of the nitroolefin class, nitroacetylenes might be prone to decompose exothermally or even be explosive. However, the conjugational effect of the nitro group should increase the stability of such systems compared with fluoroacetylenes so that their isolation should be possible.

Nitroacetylenes should give addition and cycloaddition reactions even more readily than the well-known nitroolefins^[20, 21]. Considering all these facts and conclusions the papers of Loevenich and coworkers appeared rather doubtful. In 1930 they reported the synthesis of phenyl-^[2b], ethyl- and n-propylnitroacetylene^[2a] by HBr elimination from the corresponding 1-bromo-1-nitroolefins with excess primary or secondary amines ! Even nitroolefins under these conditions add amines to give α -nitroalkylamines or are even polymerized^[22].

For the synthesis of new heterosubstituted acetylenes three simple ways are promising:

- a) substitution reactions^[23]
- b) elimination reactions^[24]
- c) isomerization of propargylic derivatives^[25].

[21] N. Levy and J.D. Rose, *Quart. Reviews* 2, 358 (1948).

[22] a) R.L. Heath and J.D. Rose, *J. Chem. Soc. (London)* 1947, 1486.

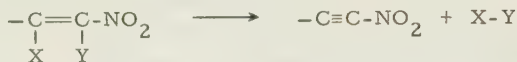
b) H. Hopf and M. Capaul, *Helv. Chim. Acta* 43, 1898 (1960).

[23] W. Ziegenbein in loc. cit. [8b], Chapter 3 (Synthesis of Acetylenes and Polyacetylenes by Substitution Reactions).

[24] G. Köbrich and P. Buck in loc. cit. [8b], Chapter 2 (Synthesis of Acetylenes and Polyacetylenes by Elimination Reactions).

[25] Review J.H. Wotiz in loc. cit. [8b], Chapter 7 (Propargylic Rearrangements).

Method b) starts already with the -C-C-NO_2 linkage found in the final product, and X-Y has to be eliminated^[24]:



The elimination of X=Y-Br can be performed in a heterogeneous way and is particularly suitable for the synthesis of base-sensitive, but either volatile or thermally quite stable acetylenes. Thus fluoroacetylene, for example, could be obtained smoothly with magnesium as dehalogenating agent^[26]. When X or Y represents a hydrogen atom, the starting compounds for nitroacetylene synthesis are 1-halo-2-nitro- and 2-halo-1-nitroolefins, resp.. This work deals only with HX eliminations from these halogeno-nitroolefins, since this route turned out successful for the preparation of the first nitroacetylenes. Halo-nitroolefins were either well known substances or, in the case of the 2-halo derivatives, they could easily be synthesized, as described in part A-I and II and part B-I, resp., of this work.

The propargylic rearrangement in method c) provided an easy large scale preparation of methylnamines from the corresponding propargylamines^[27]. With nitro compounds the propargylic or allenic rearrangement^[25, 28] might be attempted with Hünig type bases or by acid-catalysis^[29].

[26] H.G. Viehe and E. Franchimont, Chem. Ber. 95, 319 (1962).

[27] A.J. Hubert and H.G. Viehe, J. Chem. Soc. (London) C 1968, 228.

[28] This promising possibility has been pointed out to us by G. Hesse, Univ. Erlangen-Nürnberg.

While the synthesis of probably unstable systems is envisaged, the problem is eased by stabilizing substituents. Electronic stabilization of the electrophile nitroacetylene system might be achieved by an electron donor such as the dialkylamino group. Likewise, the reactive system might be blocked sterically by introducing bulky groups^[14, 30]. Both ways have been pursued. The details shall be discussed in A-I/1, B-II/1 and B-II/2.

[29] Compare, f.e., the equilibration of conjugated and non-conjugated nitroolefins by anionotropic aluminum oxide^[19a, c, e, f].

[30] Cf. C. Grundmann et al.'s successful attempts to prepare stable nitrile oxides:

a) C. Grundmann and J.M. Dean, *Angew. Chem.* 76, 682 (1964);
ibid. internat. Edit. 3, 585 (1964);

b) C. Grundmann and S.K. Datta, *J. org. Chem.* 34, 2016 (1969).

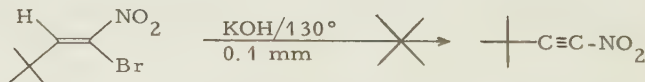
PART A. UNSUCCESSFUL APPROACHES TO NITROACETYLENES.

I. Results of other groups and revision of presumed nitroacetylene structures.

1. General.

Accidentally or intentionally, nitroacetylenes have been the subject of several investigations. "The source" of knowledge about nitroacetylenes, in general always referred to^[31], is the two papers of Loevenich et al. published in 1930^[2a, b]. Loevenich investigated the behaviour of 1-bromo-1-nitroolefins in addition reactions, especially with nucleophiles such as protic amines. On repeating this work (in part) we were not able to identify nitroacetylenes in the reaction products^[1], this shall be described in detail in paragraph A-I/2.

Another attempt at nitroacetylenes via 1-bromo-1-nitroolefins was started in 1965 at the ERA in Brussels. 1-Bromo-3,3-dimethyl-1-nitro-1-butene^[32] was distilled over dry potassium hydroxide at 130°, however, only very little volatile material could be trapped. This showed a CC triple-bond-like IR absorption, but no longer nitro group absorptions^[33]:

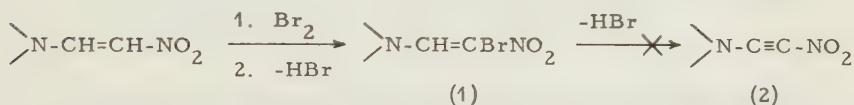


^[31] See for example [20] or T. L. Jacobs, "The Synthesis of Acetylenes", Org. Reactions 5, 12 (1949).

^[32] Prepared via 3,3-dimethyl-1-nitro-1-butene, D. L. Heywood, J. A. Durden and G. E. O'Dell, Union Carbide Olefins Division (South Charleston), unpublished results 1965.

^[33] H. G. Viehe and M. Reinstein, unpublished results 1965.

With the progress in ynamine chemistry, elaborated especially in the laboratories of J. Ficini in Paris and of H. G. Viehe in Brussels, interest arose in push-pull substituted acetylenes such as nitro-ynamines. Still unknown up to date, these were regarded as precursors of possibly stable cyclobutadienes. Bromination of an unsubstituted nitroenamine followed by dehydrobromination was carried out in R. Gompper's group at Munich, yielding the bromo-nitroenamine (1).



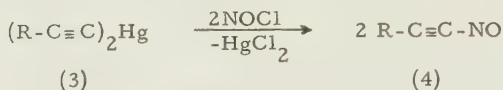
After further HX elimination under more drastic conditions, however, no nitroynamine (2) could be isolated^[34]. In K. Hafner's group apparently the same project has been pursued. In 1969 Gais, Hafner and Neuenschwander reported on the synthesis of push-pull substituted acetylenes, namely ynamines with acceptor substituents at the acetylenic carbon atom^[35]. A general formula for substituted acetylenes is given, which represents among others a nitroynamine (2), and a general synthesis of these compounds is described in the theoretical section of this paper.

[34] R. Gompper, Univ. of Munich, personal communication 1968.

[35] H. -J. Gais, K. Hafner, and M. Neuenschwander, *Helv. chim. Acta*, 52, 2641 (1969).

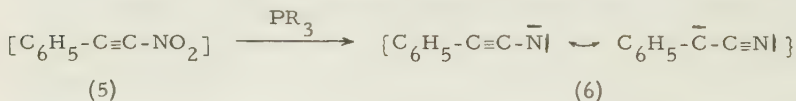
In the experimental section, however, only the preparation of (1) is given^[35] : obviously, nitroynes are still to be synthesized.

In 1968 nitroacetylenes (4) were characterized in solution by Robson, Tedder and Woodcock^[36]. This was achieved by the action of nitrosyl chloride upon dialkynylmercury (3) at -40° :



Further attempts to oxidize (4) or to obtain nitroacetylenes from (3) with nitrosyl chloride did not look promising and were abandoned^[37].

Nitroacetylenes have been regarded as a source for acetylenic nitrenes. Boyer et al. in 1967 reported on the deoxygenation of β -nitrostyrene which afforded phenylacetonitrile in low yield^[38]. To create the intermediate resonance hybrid (6) besides other compounds, phenylnitroacetylene (5) was envisaged as starting compound by which reduction with phosphite might give the cyanocarbene (6)^[39] :



[36] E. Robson, J. M. Tedder, and D. J. Woodcock, J. chem. Soc. (London), C 1968, 1324.

[37] J. M. Tedder, Univ. of St. Andrews, personal communication 1969.

[38] J. H. Boyer, W. E. Krueger, and G. J. Micol, J. Amer. chem. Soc. 89, 5504 (1967).

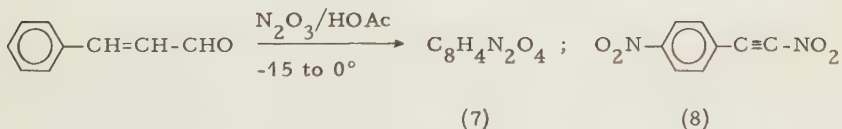
[39] J. H. Boyer, and R. Selvarajan, *ibid.* 91, 6122 (1969).

However, this approach was abandoned after attempts to prepare (5) according to Loevenich's procedure^[2b] failed^[38].

To a compound, isolated first by Wieland^[40], later by Novikov et al.^[3], the latter assigned a nitroacetylene structure. This is the subject of the following paragraph.

2. 3-Nitro-2-azachromone (4H-1,2-benzoxazin-4-one) : Structure of the presumed p-nitrophenylnitroacetylene^[4].

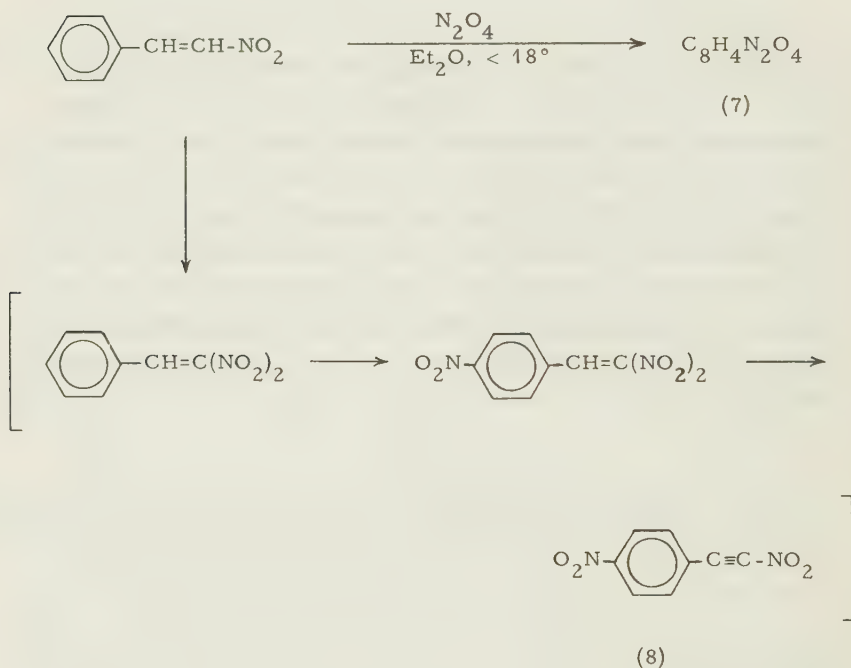
After appearance of our communication on the synthesis of the first nitroacetylene^[1] we learnt^[41] that in 1903 Wieland and in 1960 Novikov et al. had regarded a compound $C_8H_4N_2O_4$ (7)^[40, 3] as p-nitrophenylnitroacetylene (8) on the basis of elemental analysis and molecular-weight determination. Wieland had isolated this compound out of the reaction products of nitrous gases with cinnamaldehyde in a small yield. p-Nitrobenzoic acid plus other products were also formed. (7) was described as a crystalline, yellow compound having b. p. 143° (certainly a misprint instead of "m. p."), not volatile in steam distillation. Wieland gave three possible formulas for (7) including the nitroacetylene formula (8) :



[40] H. Wieland, Liebigs Ann. Chem. 328, 154 (1903). In this 102-pages-article (7) is mentioned on p. 216.

[41] We are obliged to Z. Eckstein, Techn. Univ., Warsaw, for informing us about these references.

In 1960 Novikov et al. reported the results of the reaction of β -nitrostyrene with N_2O_4 ^[3]. When the reaction was performed in ether below 18° , after 2.5 days some precipitate was collected. A second crop was obtained on cooling to -70° after the addition of methanol. Recrystallization from alcohol finally yielded yellow crystals of the compound $C_8H_4N_2O_4$ (7), m. p. $139-139.5^\circ$, 2.1%. The formation of the presumed (8) was explained as follows^[3]:



After what we already had learnt at that time from the synthesis of nitroacetylenes and from the physical and chemical properties of tert-butyl nitroacetylene, the method of formation and the stability of (7) - m. p. without dec. - could not be in accord with a compound such as (8).

We confirmed the formation of (7) besides minor amounts of p-nitrobenzoic and oxalic acid. (7) crystallized from the reaction mixture when kept for several days at -20° . The mother liquors still contained considerable amounts of β -nitrostyrene, but in the IR spectrum no triple bond absorption could be found.

Elemental analysis and molecular-weight determination were in accord with Wieland's and Novikov's values. The NMR spectrum of (7) showed a multiplet of four vicinal aromatic protons, thus indicating an ortho-disubstituted benzene derivative.

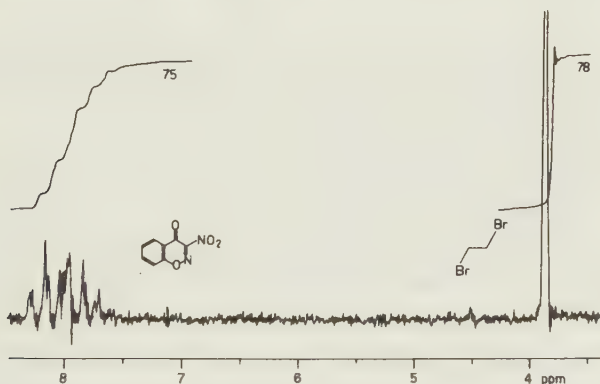
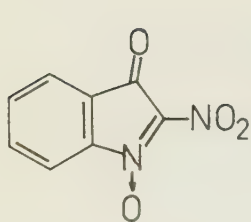
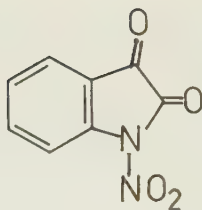


Fig. 1. NMR Spectrum of Equimolar Quantities of (7) $\equiv$ (11) and 1,2-Dibromoethane.

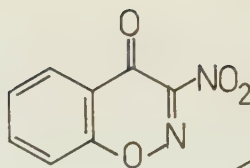
According to these facts, the four most reasonable structures for (7) were the fused heterocycles (9)-(12): an isatogen (9), an isatin derivative (10), a benzoxazinone or 2-azachromone (to show the relation with chromones) (11), and the α -nitrimine derived from cumarandione (12).



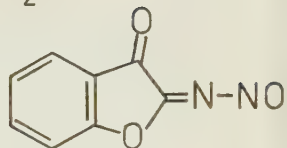
(9)



(10)



(11)



(12)

From IR, mass and UV spectra of (7), however, and from the chemical properties of (7) discussed in detail below, it turned out that only (11) fitted to all these data.

The IR spectrum of (7) exhibited strong absorptions at 1676, 1613, 1565, 1550, 1460, 1352, 1327, 1040, 813 and 771 cm^{-1} as seen in fig. 2, p. 24. IR carbonyl absorptions in isatins normally are found between 1772-1755 and 1750-1734 cm^{-1} [42] and a similar value was expected for the cumaranedione derivative (12). For 3-phenylisatogen a CO absorption at 1720 cm^{-1} was reported, the N-O group absorbed at 1385 cm^{-1} [43]. A bridged α -keto nitrimine in a 5-membered ring was found to absorb at 1753 (C=O), 1630 (C=N), 1580 and 1307 cm^{-1} (NO_2) [44].

[42] L. J. Bellamy, "Advances in Infrared Group Frequencies", Methuen & Co., Ltd., London 1968, p. 162 ff.

[43] R. J. Richman and A. Hassner, J. org. Chem. 33, 2550 (1968).

[44] T. Matsumoto and S. Yasuda, Tetrahedron Letters 1968, 5311.

On the other hand, fused 6-ring ketones show CO-absorptions at 1665 cm^{-1} (chromone^[45], at $1675\text{--}68$ (various 2, 3-dihalo-chromones^[46]), or at 1655 cm^{-1} in the case of 3-nitroflavone^[47]. The latter compound also gives rise to NO_2 vibrations at 1525 and 1370 cm^{-1} ; aromatic nitro compounds in general are known to absorb at $1548\text{--}1510$ and $1360\text{--}1340\text{ cm}^{-1}$, resp. (asym. and sym. valence stretch.)^[48].

From these IR spectral data compounds (9), (10) and (12) could be ruled out with relative certainty. The isatogen formula (9) was favoured for some time: from the reaction N_2O_4 with toluene, similar to that of Novikov described above, a side product was isolated which was proven to be 5-nitro-3-phenylisatogen^[49]. Its UV spectrum had extinctions of $4.0\text{--}4.1$ ($\log \epsilon$) while of 3-phenylisatogen $\log \epsilon$ values reached 4.5 ^[43]. However, the $\log \epsilon$ values in the UV spectrum of (7) were only 3.8 maximum (see fig. 3, p. 26). The isatogen structure (9) was excluded definitely when in the mass spectrum of (7) no peak at $M-16$ was found. This should be characteristic for any N-oxide (for the mass spectrum of (7) see fig. 4, p. 27).

[45] We thank H. Hofmann and G. Salbeck, Univ. Erlangen-Nürnberg, for the chromone spectrum.

[46] M. Le Corre, Ann. Chim. [14], 3, 193 (1968).

[47] M. Michalska, Bull. Acad. Pol. Sci., Ser. Sci. Chim. 16, 567 (1968).

[48] J. F. Brown Jr., J. Amer. chem. Soc. 77, 6341 (1955).

[49] K. N. Campbell, J. Shavel Jr., and B. K. Campbell, ibid. 75, 2400 (1953).

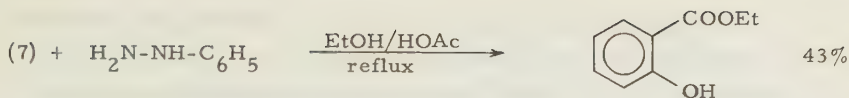
After these already conclusive spectral findings we tried to obtain positive evidence for the benzoxazinone (azachromone) structure (11) by chemical means.

In an effort to check the isotogene structure (9), the compound $C_8H_4N_2O_4$ (7) was reacted with triethyl phosphite as described for the deoxygenation of furazanes^[50], but the corresponding reduced product could not be isolated. (7) was also treated with carbonyl reagents like o-phenyldiamine (in order to convert a diketonic molecule into a quinoxaline derivative) and phenylhydrazine. The latter reaction finally gave a hint that the heterocycle was fused by means of an oxygen atom to the benzene nucleus. The reaction was carried out in the same manner as isatin hydrazones have been prepared^[51]. Any of the compounds (9), (10) or (12) should have given the corresponding hydrazone. Instead, a slightly yellow liquid isolated from the above reaction exhibited the odour of a salicylate, and in fact ethyl salicylate was identified by comparison (GLC and spectra) with a commercial sample. The ortho-O-C₆H₄-CO- fragment was also seen in the alkaline hydrolysis of (7) with 2N potassium hydroxide : (7) dissolved readily at room temperature and after work-up salicylic acid was obtained.

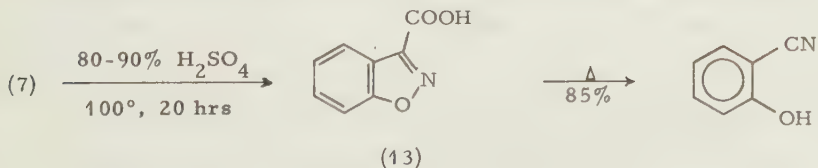


[50] C. Grundmann and H. D. Frommelt, J. org. Chem. 30, 2077 (1965), and references therein.

[51] E. Schunck and L. Marchlewski, Ber. dtsch. chem. Ges. 28, 2525 (1895).

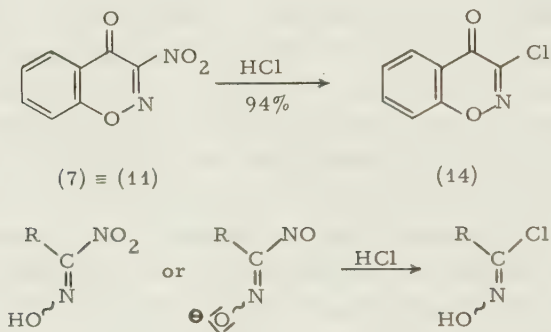


Acid hydrolysis of (7) could not be achieved under mild conditions. (7) dissolved slowly in conc. cold sulphuric acid (for changes in the UV spectrum see fig. 3, p. 26) completely in warm acid. Nevertheless, (7) was recovered unchanged upon dilution with water. Likewise, a solution of (7) in THF-25% aqueous H_2SO_4 , kept at 50° for 53 hours, showed no changes in the IR spectrum of the recovered material. Finally, with 80-90% sulphuric acid at 100° after 20 hours a reaction had taken place. The product isolated in 41% yield was a water-soluble carboxylic acid with the formula $\text{C}_8\text{H}_5\text{NO}_3$. It was identified by comparison of its melting point with literature data^[52]. Its formation was due to hydrolysis of the nitro group and rearrangement to end up with benzisoxazol-3-carboxylic acid (indoxazene-3-carboxylic acid) (13). Lindemann and Cissé, who previously had mentioned this compound, examined the ring scissions of benzisoxazoles. (13) on heating above its m. p. of 141° lost carbon dioxide to give the ring-opened product salicylonitrile^[51]. This reaction was used here to assure the structure of (13) which was also supported by its spectra.



[52] H. Lindemann and H. Cissé, *l. prakt. Chem.* [2], 122, 232 (1929).

Whereas (7) did not react with sulphuric acid in the cold, hydrochloric acid in dry ether-chloroform-ethanol smoothly converted (7) into a chloro derivative $C_8H_4ClNO_2$ within 20 hours at room temperature. This nucleophilic substitution of a nitro group in (7) is paralleled by the analogous reactions of nitrolic acids^[53a] and nitrosolic acids^[53b] which have been reported to give hydroximoyl chlorides upon treatment with hydrochloric acid:

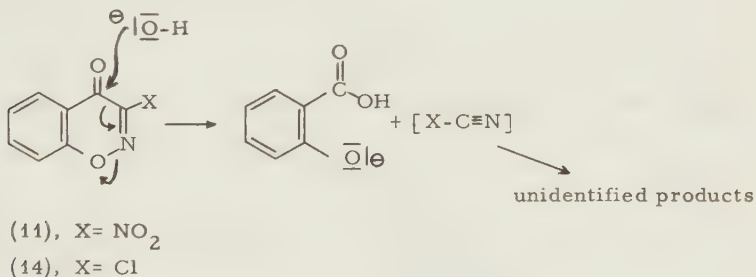


This new benzoxazinone (14) had chemical properties similar to the nitro compound (7). The reduction of (7) and (14) by lithium aluminum hydride and the platinum-catalyzed hydrogenation in different solvents resulted in complex mixtures. The behaviour of (14) towards bases and acids, however, was completely analogous to the reactions of (7). Thus treatment with KOH gave salicylic acid (69%), while treatment with conc. H_2SO_4 afforded benzisoxazol-3-carboxylic acid (13) in 62% yield.

[53] a) C. Grundmann, Fortschr. chem. Forsch. 7, 69 (1966), and personal communication.

b) loc. cit. [18], p. 378.

The systematic names for (11) and (14) are 3-nitro- and 3-chloro-4H-1,2-benzoxazin-4-one, resp. (or -2-azachromone). Only two examples of this heterocyclic class could be found in the literature. In 1926 the 7-nitro-3-phenyl derivative was synthesized in an unambiguous way. The products of alkaline degradation were benzonitrile and 4-nitro-salicylic acid^[54] which is in complete agreement with our experience on (11) and (14). Of course in our case, the nitrile fragment could not be isolated because nitrocyano O_2N-CN (a compound not yet described in the literature) and chlorocyan would be expected to decompose very fast:



Less characterized is the second 2-azachromone known up to date: 3-(2-acetoxybenzoyl)-2-azachromone (-4H-1,2-benzoxazin-4-one) was reported in 1962^[55]. Spectral data of 2-azachromones have not yet been published.

The infrared spectra of (11) and (14) are very similar as seen from the table and from fig. 2:

[54] G. Bishop and O.L. Brady, J. chem. Soc. (London) 1926, 810.

[55] E. Ziegler and E. Nölken, Mh. Chem. 92, 1062 (1962).

Table 1. Main IR absorption bands of azachromones (11) and (14).

Assignment	(11)	(14)
CO absorption	1676	1675 cm^{-1}
Ring vibrations	1613, 1460	1612, 1460
C-H def.	771	763
1350-1100 cm^{-1} region	1327, 1264	1332, 1259
	1196, 1170	1204, 1163
	1145, 1110	1140, 1100

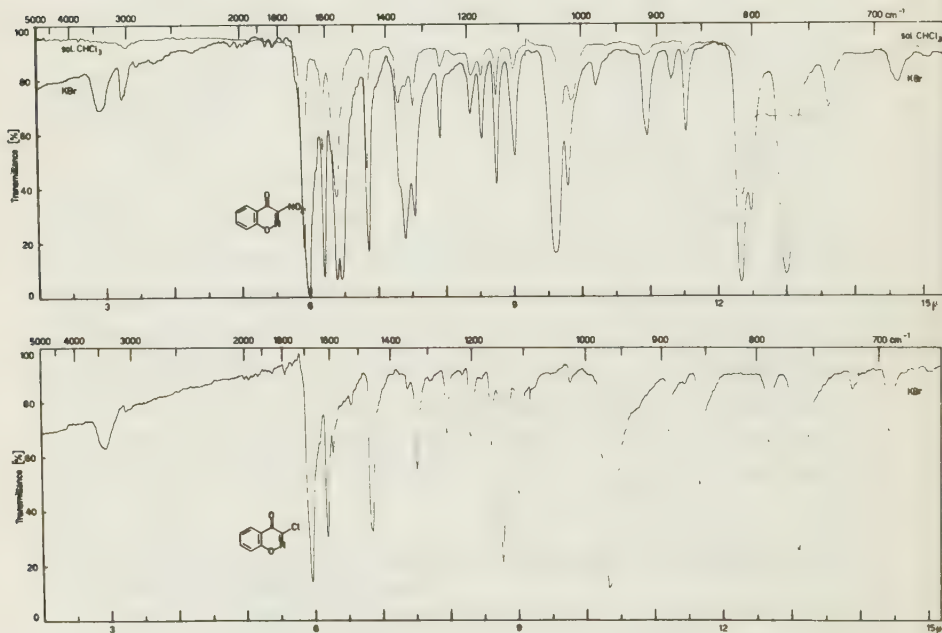
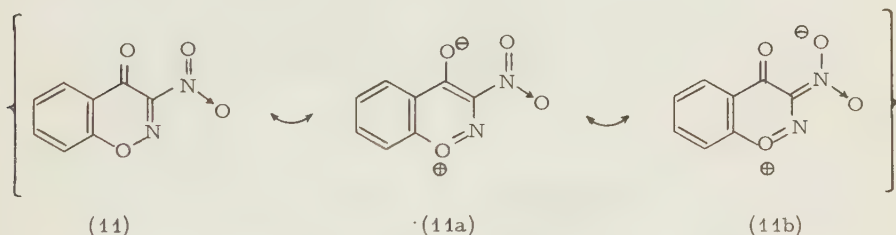


Fig. 2. IR spectra of (11) and (14).

Strong absorption bands of (11) which disappear in the spectrum of (14) are due to the nitro group: the split asymmetrical stretching vibration at 1566 and 1550, the symmetrical vibration at 1352 and probably the intense band at 813 cm^{-1} (C-N vibration?).

2-Azachromones as chromone derivatives represent 10 π electron systems. In (11 a, b) the negative charge is stabilized by the carbonyl group as well as by the nitro group. This may be rationalized by the following mesomeric structures:



Both 2-azachromones (11) and (14) gave yellow solutions on dissolving in conc. sulphuric acid at 20°. The UV spectrum of (14) then showed only slight changes compared with the methanolic solution. However, an additional band appeared at 384 nm ($\log \epsilon = 3.36$), see fig. 3. Greater differences are to be seen in the absorptions of the nitro compound (11). Here too, a new band arose at 400 nm (3.2). The nitro group should contribute to stabilize protonated species as shown below:



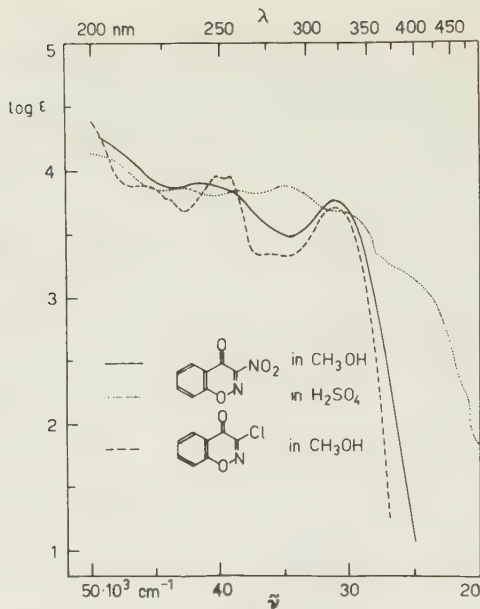


Fig. 3. UV spectra of (11) and (14) in methanol and in conc. sulphuric acid.

These protonations were reversible as already noted (p. 21). Efforts to prepare pyrylium-like oxonium salts by alkylation with methyl iodide or chloroacetone, however, failed.

The electron-impact fragmentation patterns of (11) and especially of (14) – see figs. 4, 5, 6 – further proved the assigned structures. The major decomposition pathways, as calculated from metastable analysis, are given in the following schemes (figs. 5, 6).

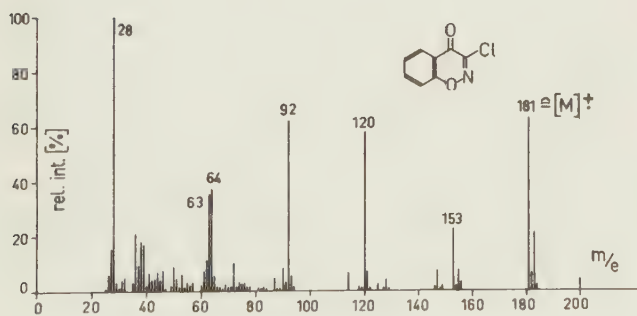
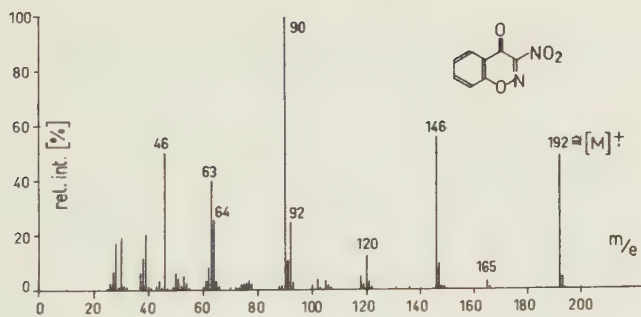


Fig. 4. Mass spectra of (11) and (14).

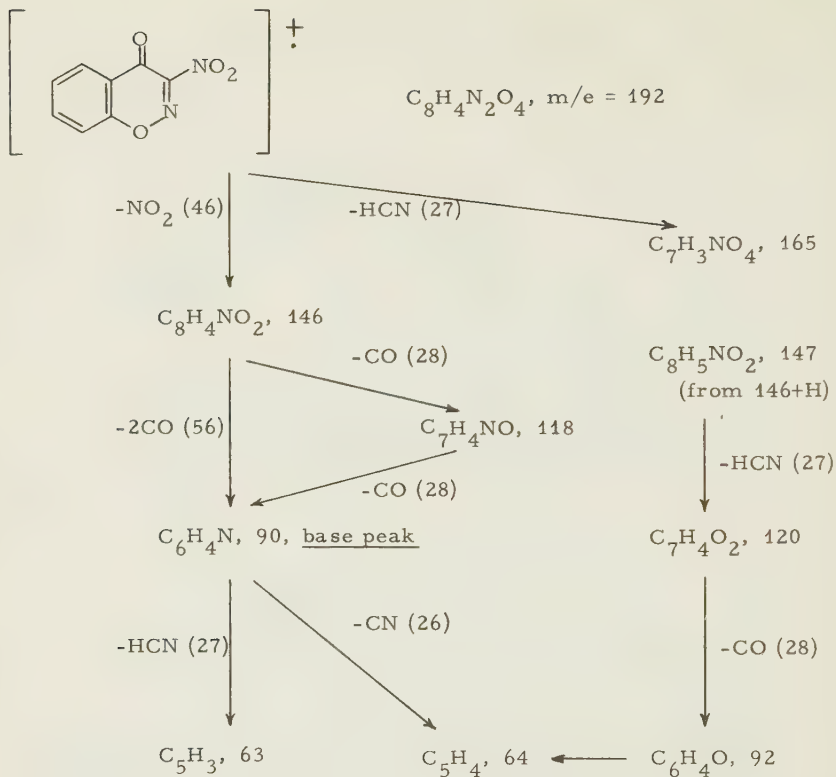


Fig. 5. Fragmentation scheme for (11).

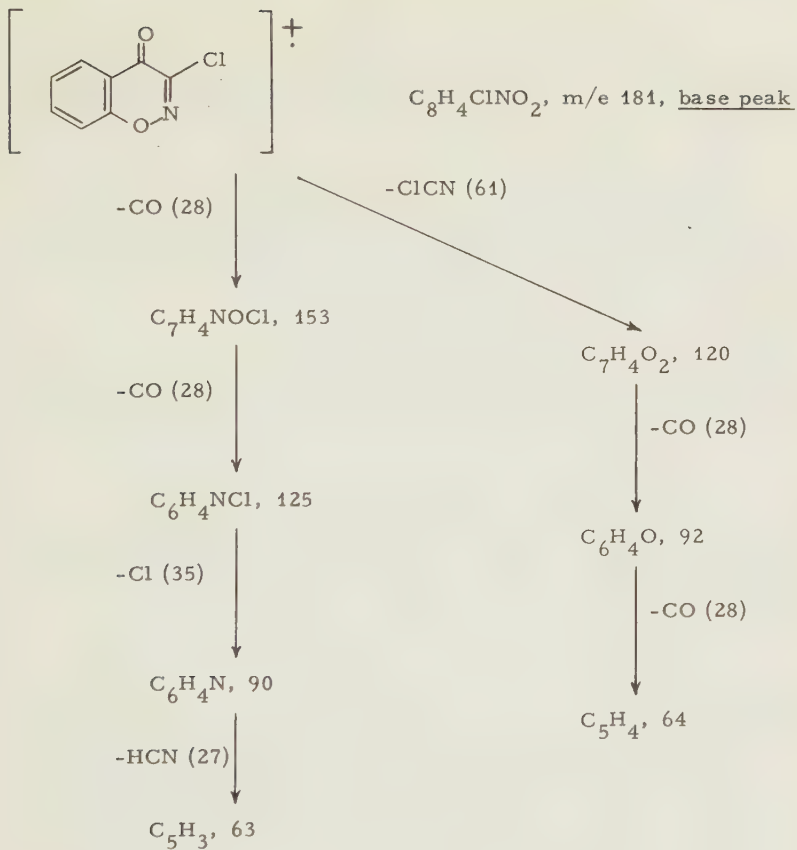


Fig. 6. Fragmentation scheme of (14).

The loss of ClCN was most indicative for the assigned structure (14). The degradation paths of (11) and (14) became similar beginning with ions 120 and 90 which occurred in both spectra.

To summarize, the compound $C_8H_4N_2O_4$ (7) isolated from the action of N_2O_4 on β -nitrostyrene and incorrectly formulated as p-nitrophenyl-nitroacetylene, has been established to be a derivative of 4H-1,2-benzoxazin-4-one (2-azachromone)^[56, 57].

3. Verification of previous attempts at nitroacetylene synthesis from 1-bromo-1-nitroolefins^[1]

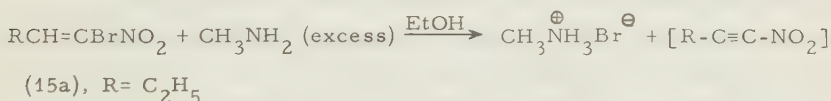
It has already been mentioned that in 1930 Loevenich and coll. erroneously reported on nitroacetylenes. The first paper^[2a] dealt with the behaviour of 1-bromo-1-nitro-1-butene and -pentene (15a) and (15b), resp., in addition reactions, especially additions of ammonia and amines. The corresponding adducts were described

[56] From a letter of S.S. Novikov and V.M. Belikov, Zelinski Inst. of Org. Chemistry, Moscow, who had received a preprint of [4]: "We had ascribed the structure of p-nitrophenylnitroacetylene ... only on the basis of its analysis and its similarity to the compound obtained by Wieland. We had obtained this compound as a by-product with very low yield and had not investigated it more in detail. We are pleased that its structure is now ascertained".

[57] Kerber and coll., State Univ. New York, who had worked on unsaturated aliphatic nitro compounds for some time^[58], had tried to synthesize nitroacetylenes and thus became faced with the structure of (7), too. Structure (9) was favoured before learning our experimental facts that admitted only formula (11).

[58] For example on "Nitrocyclopentadiene": R.C. Kerber and M.J. Chuck, J. org. Chem. 32, 1329 (1967).

either as unstable and eliminating ammonium salts on storage at room temperature, or that HBr elimination took place instantaneously. The resulting undistillable oils were designated as nitroacetylenes. For example, methylamine was bubbled into an ethanolic solution of (15a) until saturated. After some hours at room temperature the mixture was treated with water-ether. The ethereal phase was dried and evaporated to leave a thin oil with a very pungent odour. This liquid added bromine and decolorized Baeyer's reagent. On attempted distillation an explosive decomposition occurred. Nitrogen analysis gave 13.51%, calc. 14.14^[59]; no more halogen was reported to be found in this liquid. After some time the oil formed a viscous resin. This is represented as follows:



After refluxing (15b), R = n-C₃H₇, with diethylamine in ethereal solution and filtering, the ether and excess diethylamine were drawn off to leave a dark-red, viscous, non-volatile oil. The nitrogen analysis was 11.46%, calculated 12.39% ; molecular weight found 131.3, theoretical value 113.

In the second paper the analogous reactions of 2-phenyl-1-bromo-1-nitroethylene (15c), R = C₆H₅, were investigated. With diethylamine and aniline no addition products were obtained. Instead, direct elimination to "phenylnitroacetylene" (16) was reported.

[59] It is not clear why no CH analysis of any of the presumed nitroacetylenes was reported.

According to the prescription to prepare (16), the bromonitroolefin (15c) had to be refluxed for 8 hours with a slight excess of diethylamine. After filtering off the precipitated salt and removal of the solvent a dark, deep red, undistillable oil resulted. N analysis and molecular-weight determination were in accord with the calculated values (found 9.62, 148.4 ; theor. 9.52, 147).

The chemical properties of nitroolefins^[20-22] and the reactions of nitroacetylenes described in part B of this study, are contradictory to the properties of these isolated undistillable oils (IR spectroscopy too was not known at that time). Unfortunately, no paper dealing with the verification of these results could be found in the literature, when we started this work. We examined that part of the former investigations dealing with the phenyl compound, because in the nitro olefin series the phenyl derivative β -nitrostyrene is less readily polymerized by bases than the lower alkyl derivatives of this class^[60], and the same should be expected in the acetylene series.

When (15c) was treated with diethylamine according to the lit.^[2b], about 50% of the theoretical amount of diethylammonium bromide precipitated. After work-up the residual dark red-brown oil still contained starting material. TLC analysis showed at least three other products. Nevertheless, the crude reaction mixture gave a nitrogen analysis quite close to the calculated value (8.89 vs. 9.62%). The reaction was followed by IR which showed the absence of absorptions in the triple bond region at any time. The product distilled in part over a wider temperature range at 0.1 mm, but only benzaldehyde and starting product (15c) could be found in the distillate.

^[60] D.E. Worrall, J. Amer. Chem. Soc. 49, 1598 (1927).

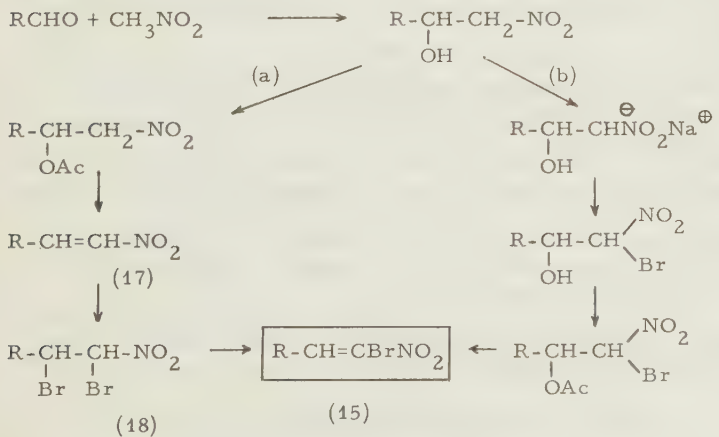
From the decreasing stability of the nitroacetylenes, when passing from tert-butyl via the i-propyl to the n-propyl derivative (see B-II and III), it seemed impossible that any of the supposed nitroacetylenes [2a, b] could survive such reaction conditions. The exothermal reactions of the sterically crowded tert-butyl nitroacetylene with primary and secondary amines showed that amines added immediately to the triple bond.

Boyer and Selvarajan's fiasco in preparing phenylnitroacetylene^[38] according to the literature^[2b] has already been specified in A-I/1. Moreover, further attempts to arrive at nitroacetylenes starting with 1-bromo-1-nitroolefins, were unfruitful, see A-II/3.

II. Own Results with 1-bromo-1-nitroolefins.

1. Synthesis of 1-bromo-1-nitroolefins.

1-Bromo-1-nitroolefins of the general formula $RCH=CHNO_2$ (15) have been prepared according to two slightly different methods^[6f]:



(15b), $R = C_3H_7$

(15c), $R = C_6H_5$

(15d), $R = C(CH_3)_3$

Method b) seemed more difficult because the isolation of the water-soluble sodium salts of the nitroalcohols usually involves some loss. The starting materials for method a), β -nitrostyrene (17c), 1-nitro-1-pentene (17b)^[62] and 3,3-dimethyl-1-nitrobutene (17d),^[19a, 32, 63] were easily accessible.

The phenyl derivative (15c) was synthesized^[64-66] to check the literature reports of phenylnitroacetylene synthesis (see preceding paragraph). The tert-butyl compound^[32] (15d) was prepared, because HBr elimination from a 1-bromo-1-nitroolefin should be examined and the expected t-butyl nitroacetylene had been shown to be quite stable (see B-II, III). The n-propyl derivative^[2a] (15c) should serve as a model compound to compare the spectral data (NMR) and to determine the configuration of these 1-bromo-1-nitroolefins.

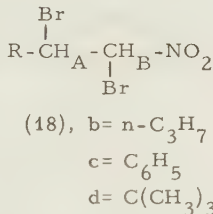
The addition of bromine to the nitroolefins (16) gave the corresponding 1,2-dibromo-1-nitroethanes (18) in 90-94% yield. From (18c), hydrogen bromide was removed by means of ethanolic sodium acetate^[65]. Similarly HX was eliminated from (18b) with triethylamine and from (18d) by stirring with an α -picoline solution in benzene^[32]. These eliminations proceeded at room temperature and the resulting yellow, lachrymatory 1-bromo-1-nitroolefins were obtained in 80-90% yield.

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- [61] In part reviewed in a) G.A. Shvekgeimer, V.A. Smirnyagin, R.A. Sadykov, and S.S. Novikov, Russ. Chem. Reviews 37, 351 (1968) and in [21].
- [62] E. Schmidt and G. Rutz, Ber. dtsch. chem. Ges. 61, 2142 (1928).
- [63] A. Hassner, J.E. Kropp, and G.J. Kent, J. org. Chem. 34, 2628 (1969), prepared this nitroolefin from 3,3-dimethyl-1-butene via the NO₂-iodine adduct.
- [64] B. Priebs, Liebigs Ann. Chem. 225, 319 (1884); the correct structure was assigned later^[59].
- [65] J. Thiele and S. Haeckel, ibid. 325, 1 (1902).
- [66] Compare the analogous reactions performed by D.E. Worrall, J. Amer. Chem. Soc. 62, 3253 (1940) with 1,4-bis-(β -nitrovinyl)-benzene.

As was (18c), the phenyl derivative (15c) was solid. The alkyl derivatives (18b), (18d) and (15b), (15d) were liquids.

2. Stereochemistry of 1, 2-dibromo-1-nitroethanes and 1-bromo-1-nitroolefins.

The NMR spectra of (18b) and (18c) show vicinal coupling constants of ca. 10 and 10.2 cps, resp. This is much higher than expected for such systems. Usually values of 6-7 cps are found when free rotation can occur and all conformers are equally populated^[67]. Bulky substituents such as tert-butyl, iso-propyl, phenyl, iodine or bromine are known to impose severe conformational restraints. From di-tert-butylcyclohexanes, for example, the cis isomer with equatorial t-butyl groups has been reported to predominate in a 97:3 ratio over the trans isomer in the equilibrium at 493°^[68]. Moreover, the trans isomer has been shown to avoid the axial conformation of the t-butyl group on changing to the boat form of cyclohexane^[68]. In acyclic molecules as 2-substituted 3,3-dimethylbutanes (19) energy differences of 0.8 (X= CN) to 2.3 kcal/mole have been calculated from the temperature dependence of the vicinal coupling constants^[69]. J values were $J_t = 13.6-14.3$ for the trans protons and $J_g = 3.7-4.2$ cps for the gauche vicinal coupling (protons in equatorial position). Jackmann and Kelly very recently investigated 1, 2-dihalo-substituted tert-butylethanes (3,3-dimethylbutanes). They found $J_t = 9.1$ and $J_g = 3.1$ cps, resp., with predominant, if not exclusive population of the rotamer (20)^[70].

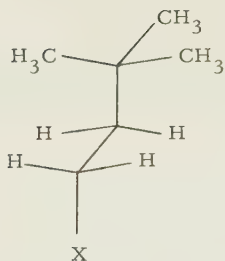


[67] loc. cit. [16], p. 52 f.

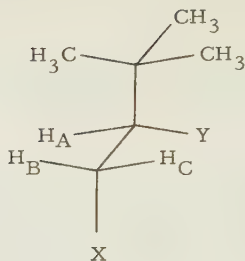
[68] N.L. Allinger and A. Freiberg, J. Amer. Chem. Soc. 82, 2393 (1960).

[69] G. Whitesides, J. Sevenair, and R. Goetz, ibid. 89, 1135 (1967).

[70] L.M. Jackman and D.P. Kelly, J. Chem. Soc. (London), B 1970, 110.

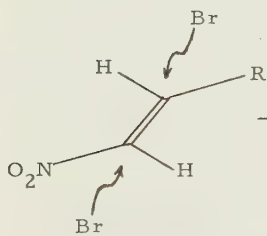


(19)

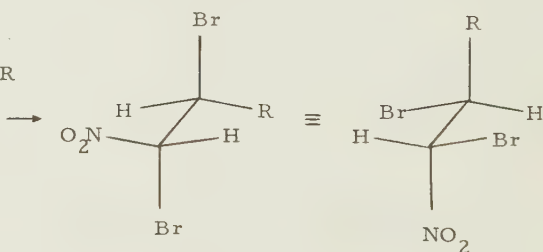


(20)

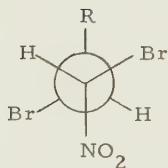
Starting with trans-nitroolefins^[71] bromine addition which proceeds in general trans^[72] leads to the erythro isomer^[73] (18). In accord with the above findings, the sterically most favoured conformer (18) I should be by far the more populated when compared with the gauche rotamers II and III.



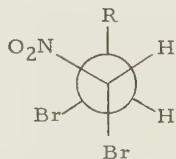
(17)



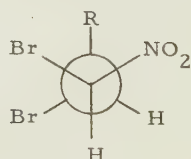
(18) I



(18) II



III

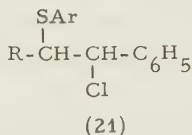


IV

The observed values of 10 and 10.2 cps, resp. for the n-propyl and the n-phenyl compounds (15b) and (15c) resp., are in excellent agreement with this. However, on passing to the analogous compound with R= tert-butyl, two rotamers were present according to the NMR spectrum, ratio 2:1. The conformer with the higher coupling constant 7.5 cps is still predominant, but other isomers II and/or III with $J = 2.5$ cps are substantially populated. As the signals of the two rotamers appear well separated at room temperature, it must be concluded that rotation about the CC single bond is restricted or that it is very slow compared to the recording time. There are some cases known where rotamers with gauche standing bulky groups are much more stable than expected from Dreiding models.

-
- [71] a) n-Propyl derivative (17b): H.G. Viehe and V. Jäger, unpublished results.
 b) Phenyl derivative (17c): N.S. Bhacca, L.F. Johnson and J.N. Shoolery, High Resolution NMR Spectra Catalog I, Varian Ass., California, Palo Alto, and E.O. Bishop R.E. Richards, Mol. Phys. 3, 114 (1960).
 c) t-Butyl derivative: see [19a] and [57].
- [72] If bromine added in a cis manner as a consequence of acid catalysis, the results of the following discussion were similar as stated for trans addition. However, an E2 process is then possible from the most stable threo rotamer, cf. p. 43.
- [73] For a recent review on "The Stereochemistry of Electrophilic Additions to Olefins and Acetylenes", see R.C. Fahey, Topics Stereochem. 1968, 280 f.
- [74] A.A. Bothner-By and C. Naar-Colin, J. Amer. Chem. Soc. 84, 743 (1962).

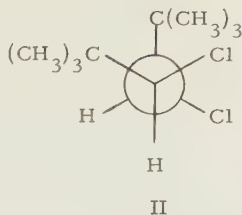
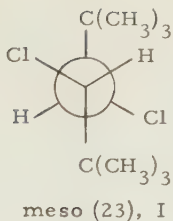
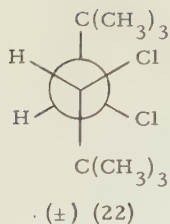
Curiously enough, in NMR studies of acyclic pairs of diastereoisomers for the compounds with isopropyl or other bulky substituents, large vicinal coupling constants have been found. The analogous tert-butyl derivatives, however, give rise to small J values. For example, in the erythro compounds (21) J is 10.7 cps for R= isopropyl, but for R= tert-butyl the coupling constant is 4.7 cps^[74].



Similarly, the (±)-isomer (22) according to the coupling constant J= 0.8 cps of the vicinal protons must be considered to have trans tert-butyl groups which corresponds to 2.7 D found for the dipole moment. However, in the meso isomer (23), the J value of 5.2 cps^[75] and the dipole moment of 1.9 D^[76] show considerable population of the seemingly unfavourable conformation II. With more experimental facts available, the reasons of this interesting phenomenon might be rationalized generally.

[75] R.C. Fahey, J. Amer. Chem. Soc. 88, 4681 (1966).

[76] D.C. Best, G. Underwood and C.A. Kingsbury, Chem. Comm. 1969, 627.



The structures of the synthesized 1-bromo-1-nitroolefins (15 b, c, d) have been assigned by NMR, UV and IR spectral data. The NMR peaks of the olefinic protons are located at 7.60, 8.62 and 7.75 ppm ($\delta_{\text{TMS}}=0$). Their position permits one to distinguish between different stereoisomers, when the method of "Estimation of Chemical Shifts of Olefinic Protons Using Additive Increments" is applied. This method was developed independently by Tobey^[77] and a Swiss group^[78] and has recently been used to calculate the increments of the nitro group^[79]. The elimination of HBr from (18) may lead to two different isomers, (15) I and (15) II. Estimation of the respective chemical shifts gives the results listed below. As this procedure is used throughout this work when the NMR spectra and stereochemistry of trisubstituted olefins are discussed, it shall be demonstrated here in detail.

[77] S. W. Tobey, J. org. Chem. 34, 1281 (1969).

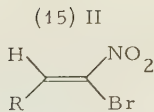
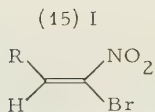
[78] a) C. Pascual, J. Meier and W. Simon, Helv. Chim. Acta 49, 164 (1966).

b) U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon and S. Sternhell, Tetrahedron 25, 691 (1969).

c) ibid. 25, 2023 (1969)..

[79] a) loc. cit. [19a], p. 29 ff.

b) G. Descotes, Y. Bahurel, M. Bourillot, G. Pingeon and R. Rostaing, Bull. Soc. Chim. France 1970, 282.



(15b) R= n-C₃H₇ ; (15d) R= C(CH₃)₃;

base value (chemical

shift of ethylene)	5.25		5.25
alkyl gem	0.45	alkyl gem.	0.45
Br cis	0.45	Br trans	0.55
NO ₂ trans	<u>0.6</u>	NO ₂ cis	<u>1.4</u>
	6.75		7.65

found for (15b) δ = 7.60 (in CCl₄)

(15c) δ = 7.75 ppm (in CCl₄)

(15c), R= C₆H₅:

base value	5.25		5.25
aromatic gem	1.38	aromatic gem	1.38
Br cis	0.45	Br trans	0.55
NO ₂ trans	<u>0.6</u>	NO ₂ cis	<u>1.4</u>
	7.68		8.58

found : δ = 8.62 ppm (in CDCl₃).

As the standard deviation of this method is about 0.2 ppm, the above results strongly favour structure (15) II for all the 1-bromo-1-nitroolefins prepared. Structure (15) II is further supported by the chemical shift of the allylic methylene protons in the NMR spectrum of (15b). In trans-1-nitro-1-propene the methyl group

shows signals centred at 1.95 ppm^[19a, 79b, 80], whereas the methyl group of the cis isomer appears at 2.15 ppm^[19a]. As can be seen also in B-I/4, allylic protons cis to a nitro group are always more strongly deshielded than trans-allylic protons and their signals appear at lower field. In (15b) the quartet of the allylic protons is located at 2.4 ppm which is a shift of only 0.1 ppm downfield when compared with trans-1-nitro-1-pentene [71a]. A shift of at least 0.2, more probably 0.3-0.5 ppm is expected (see B-I/4). This view of the trans C-C=C-NO₂ unit in the derivatives of (15) prepared is also suggested by UV and IR spectra, especially of (15d). As discussed further in part B-I/4, UV spectra of compounds with cis nitro and tert-butyl groups show considerable deviations from those of less bulky substituted halonitroolefins. This is due to steric crowding that hinders coplanarity and thus complete conjugation.

The above steric interaction can be observed in the IR spectra, too. The most characteristic feature here is a shift of the C=C valence vibration together with characteristically reduced intensity of this band, when tert-butyl and nitro group are in cis position. These effects of steric hindrance are absent in the IR and UV spectra of the tert-butyl compound (15d). Thus additional evidence for the assigned trans structures (15) II is provided (cf. UV spectrum of (15d), fig. 12, p. 69).

-
- [80] a) Yu.V. Baskov, T. Urbanski, N. Witanowski, and L. Stefaniak, *Tetrahedron* 25, 1519 (1964).
 b) H.J. Fröhlin, K.R. Loos, and H.H. Günthard, *Helv. Chim. Acta* 51, 1593 (1968).

The elimination of HX (X= halogen, acyl etc.) under very mild conditions is a general feature of 2-X-1-nitroalkanes with an α hydrogen. In our case, a concerted E2 elimination proceeding from (18) II, the only conformer with H and Br anti, should yield the corresponding nitroolefins with cis alkyl and nitro groups (15) I. In fact, as discussed above, the trans isomers (15) II are formed exclusively. It is therefore probable that the elimination follows an E1cb-type mechanism with intermediate formation of a well stabilized nitronate anion^[81].

It is known from equilibrium measurements of cis- and trans-1-nitro-1-propene that the trans isomer at room temperature is favoured by 2 kcal (corresponding to a 97:3 concentration ratio) [19e, 82]. Very likely this is due to the unfavourable steric interaction of cis methyl and nitro groups.

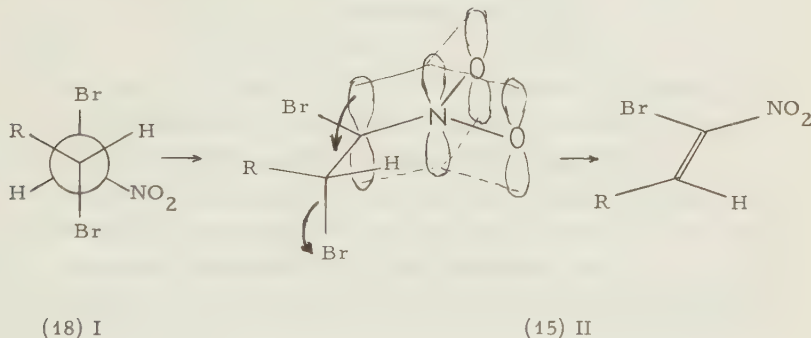


Judging from bond lengths^[79b, 83], the van der Waals interaction of a nitro group upon an ethylenic cis substituent is more important than that of bromine. Moreover, bromine is more prone to deformation than the relatively rigid atom groups formed by first period elements. It can be concluded that the situation is similar in 1-bromo-1-nitroolefins. The bulkier nitro group is less stable cis

[81] For a review on the E1cB mechanism with some examples of eliminations to nitroolefins, see D.J. McLennan, Quart. Reviews 21, 490 (1967).

[82] loc. cit.^[19a], p. 92 ff.

to an alkyl group than bromine is, thus rendering the trans-olefins (15) II the more stable isomers. Bearing this in mind, the intermediate carbanion then tends to eliminate bromine so that the most stable isomer (15) II is formed:



Evidence for E1cB eliminations to nitroolefins is numerous in the literature^[81]. In one case, even the intermediate carbanion has been isolated^[84].

3. Attempted nitroacetylene synthesis from 1-bromo-1-nitroolefins.

1-Bromo-1-nitroolefins (15) eliminate hydrogen bromide when treated with secondary or primary amines as reported by Loevenich et al.^[2] and discussed in A-I/3. Cold methanolic potassium hydroxide, however, added to (15a) and (15b) to yield the corresponding 2-methoxy

[83] a) L.F. Fieser and M. Fieser, "Organische Chemie", 2nd. ed., Verlag Chemie GmbH, Weinheim 1968, p. 1826.

b) L. Pauling, "Die Natur der chemischen Bindung", 2nd ed., Verlag Chemie GmbH, Weinheim 1964, p. 245 f.

[84] A. Berndt, Angew. Chem. 81, 567 (1969), *ibid.* internat. Edit. 8, 613 (1969).

compounds without elimination of HBr. Sodium methoxide reacted exothermally with (15a) to give the sodium salt of 2-methoxy-1, 1-dinitro-butane^[2a]. It seems clear from these facts that under such conditions 1-bromo-1-nitroolefins first add the nucleophilic bases and then several reactions follow.

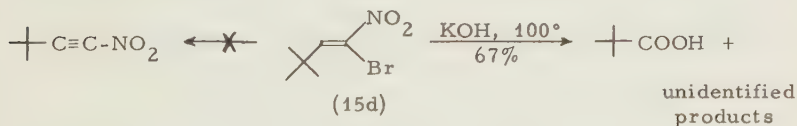
When 1, 2-dibromo-2-phenyl-1-nitroethane (18c) was treated with excess triethylamine, the first mole of hydrogen bromide was readily removed. However, even after 20 hours of reflux in ether according to the IR spectrum only bromo-nitroolefin (15c) was present. In the triple bond region no absorption could be observed. Likewise, (15c) and sodium acetate in DMF gave a dark-brown solution, but IR spectroscopic control showed no triple bond either.

If nitroacetylenes were formed in homogeneous solution, they would be destroyed by excess base. Looking for a strong base that allowed heterogeneous conditions, solid potassium hydroxide was considered to be suitable^[24]. Positive results have already been obtained in these laboratories in preparing extremely base-sensitive fluoroacetylenes by distillation of their congeners over KOH heated up to 130°^[85, 86]. When the bromonitroolefin (15c) was dropped on dry potassium hydroxide at 130° and attached to high vacuum, no volatile product could be collected in a cool trap. Extraction of the KOH-filled glass tube with ether brought only minor quantities of a material without nitro groups in the IR.

[85] Synthesis of tert-butylfluoroacetylene: H.G. Viehe, R. Merényi, J.F.M. Oth and P. Valange, *Angew. Chem.* 76, 888 (1964); *ibid. internat. Edit.* 3, 747 (1964).

[86] Synthesis of fluorochloroacetylene: S.Y. Delavarenne and H.G. Viehe, *Chem. Ber.* in press. Presented at the 3rd International Symposium on Fluorine Chemistry, Munich, Sept. 1965.

Finally, the tert-butylnitroolefin (15d) was prepared because the corresponding tert-butylnitroacetylene had proved to be quite stable (see B-II, III). (15d) remained unchanged by α -picoline at room temperature as seen from its preparation. Therefore, in another attempt (15d) was distilled over potassium hydroxide at 100° as described for the synthesis of tert-butylnitroacetylene^[1] in chapter B-II. Again quality (IR) and quantity of the distilled material were not worth speaking of, but the KOH pellets were covered by a pale-green layer. After work-up this was identified as pivalic acid. Perhaps this derived from addition of the hydroxide anion to the double bond, C-C cleavage (retro-aldol) and oxidation of the aldehyde group by the nitro group from the other fragment formed. Certainly HX elimination is not the first step in this reaction sequence, because t-butylnitroacetylene turned out to be completely unaffected on distillation over KOH at 100°. Moreover, this procedure was usually applied to the purification of the nitroacetylene.



PART B. SYNTHESIS, PROPERTIES AND REACTIONS OF NITROACETYLENES.

I. Synthesis and Stereochemistry of 2-Halo-1-nitroolefins.

1. General

As discussed in the preceding chapter, HBr eliminations from 1-bromo-1-nitroolefins did not result in nitroacetylenes. This is probably due to the favoured addition of base to the electrophilic double bond. In 2-halo-1-nitroolefins the olefinic proton is geminal to the nitro group and ought to be more acidic than the β -cis proton in 1-halo-1-nitroolefins. Although the acidities of these protons have not yet been compared directly, this is indicated by the NMR spectrum of nitroethylene^[79b, 80b, 87] and the increments of the nitro group^[79], Cp. part A-II/2. The chemical shifts for the trans, cis and geminal protons of nitroethylene are 5.9, 6.6 and 7.1 ppm, what reflects approximately the relative acidities of these protons.

The addition of NO_2X to olefins with $\text{X} = \text{OAc}$ ^[88], NO or NO_2 ^[89-94], Cl ^[95], Br ^[96], and I ^[63, 97-99] resp., and subsequent HX elimination has found various applications to prepare nitroolefins.

[87] W. Brügel, T. Ankel and F. Krückeberg, Z. Elektrochem., Ber. Bunsenges. physik. Chem. 64, 1121 (1960).

[88] F.G. Bordwell and E.W. Garbisch Jr., J. Amer. Chem. Soc. 82, 3588 (1960).

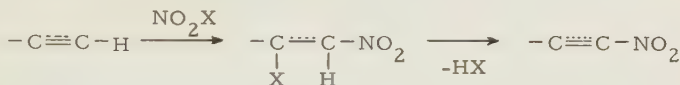
[89] a) N. Levy, C.W. Scaife and A.E. Wilder-Smith, J. Chem. Soc. (London) 1948, 52.

b) H. Baldock, N. Levy and C.W. Scaife, *ibid.* 1949, 2627.

Although the corresponding additions of NO_2 , $\text{X-X} = \text{NO}$ or NO_2 [49, 100-102], Cl [95 a, b, 103-105], I [97] - to CC triple bonds have been described, this work was done mostly with disubstituted acetylenes as substrates.

-
- [90] a) H. Shechter and F. Conrad, J. Amer. Chem. Soc. 75, 5610 (1953)
 b) H. Shechter, Record Chem. Progress 25, 55 (1964).
 c) H. Shechter, J.J. Gardikes, T.S. Cantrell, and G.V.D. Tiers, J. Amer. Chem. Soc. 89, 3005 (1967).
- [91] A. Dornow and A. Müller, Chem. Ber. 93, 41 (1960).
- [92] M. Hauptschein and R.E. Oesterling, J. org. Chem. 28, 1279 (1963).
- [93] G.A. Bonetti, C.B. Desavigny, C. Michalski, and R. Rosenthal, ibid. 30, 237 (1968).
- [94] A. Berndt, Tetrahedron 25, 37 (1969).
- [95] a) W. Steinkopf and M. Kühnel, Ber. dtsch. Chem. Ges. 75, 1323 (1942).
 b) H. Brintzinger and K. Pfannstiel, Z. anorg. Chem. 255, 326 (1948).
 c) H. Shechter, F. Conrad, A.L. Dalton, and R.B. Kaplan, J. Amer. Chem. Soc. 74, 3052 (1952).
- [96] J.C.D. Brand and I.D.R. Stevens, Chem. and Ind. 1956, 456.
- [97] T.E. Stevens and W.D. Emmons, J. Amer. Chem. Soc. 80, 338 (1958).
- [98] M. Braid, E.A. Tyczkowski, and D.M. Gardner, J. Org. Chem. 28, 1279 (1963).
- [99] a) A. Hassner in L. Fieser and M. Fieser, "Reagents for Organic Synthesis", J. Wiley & Sons, Inc., New York 1967, p. 757.
 b) J.E. Kropp, A. Hassner, and G.J. Kent, Chem. Comm. 1968, 906.

In a few papers has a terminal acetylene - phenylacetylene - been reacted with NO_2Cl ^[95a, 102, 105], NOCl ^[103] or NO_2 -iodine^[97] to yield addition products suitable for our purpose.



Until now no addition products have been characterized starting with terminal alkylacetylenes. Schlubach and Rott reported on the reaction of 1-propyne with N_2O_4 : only unstable oils, the formation of acetic acid and even explosions have been observed^[101]. With acetylene itself as starting product, Campbell et al. stated that very slow addition occurred. Unfortunately no definite reaction product could be isolated^[49].

2. Reaction of nitryl chloride with terminal acetylenes.

The addition of NO_2X to olefinic double bonds has been proved to proceed by a radical mechanism, when carried out without solvents or in solvents such as ether, methanol or chloroform^[95c]. NO_2 always adds to the terminal carbon. The intermediate radical then may exchange chlorine with NO_2Cl to yield the chloro-nitro compound and nitrogen dioxide:

[100] H. Wieland and E. Blümich, Liebigs Ann. Chem. 424, 100 (1921).

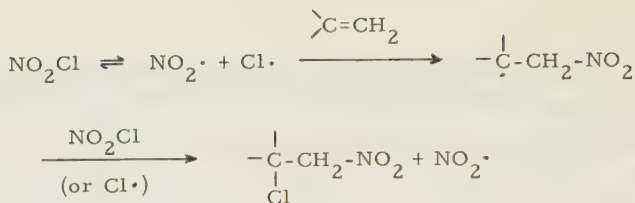
[101] H.H. Schlubach and W. Rott, Liebigs Ann. Chem. 594, 59 (1955).

[102] J.P. Freemann and W.D. Emmons, J. Org. Chem. 79, 1712 (1957).

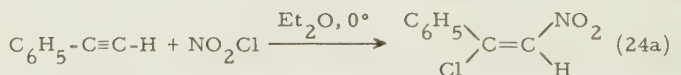
[103] R. Perrot and R. Berger, C.R. hebdomadaire des Séances Acad. Sci. 235, 185 (1952).

[104] H.H. Schlubach and A. Braun, Liebigs Ann. Chem. 627, 28 (1959).

[105] I. Iwai, K. Tomita, and J. Ide, Chem. Pharm. Bull. (Tokyo) 13, 118 (1965); C.A. 62, 14541e (1965).



Thus no stereospecificity should be observed when phenylacetylene is treated with nitryl chloride under similar conditions. In the most recent paper dealing with this reaction, Iwai and coworkers described the isolation of solid trans-2-chloro-2-phenyl-1-ethylene in 40-50% yield^[105]. Besides small quantities of 2,2-dichloroacetophenone, benzoic acid and a mixture of chlorinated styrenes, a very small amount of liquid cis-2-chloro-2-phenyl-1-nitroethylene was found. The latter was identified by its IR spectrum and comparison with an authentic sample isolated from the action of NOCl on phenylacetylene [105].



+ chloro-styrenes

On repeating Iwai and coworkers' procedure 35% of the solid isomer were obtained from the first crop. No effort was made to increase the yield by work-up of the mother liquor or to isolate other products therein. IR and UV spectra of (24a) were in accord with those already reported^[105]. The UV spectrum of (24a) is given in fig. 11, p. 69. For a detailed discussion of the geometric isomerism in 2-halo-1-nitro-olefins see B-I/4.

When tert-butylacetylene was reacted similarly with nitryl chloride in abs. ether at 0°, there resulted a complex mixture of at least 11 other compounds besides much starting material, as seen from GLC analysis. In order to obtain a less complicated ionic reaction, carbon disulfide was used as solvent with AlCl_3 as catalyst. In this case dark, resinous products were formed. The project apparently not being of great promise was abandoned in favour of the NO_2 -iodine additions.

3. Addition of NO_2 -iodine to terminal acetylenes.

The addition of NO_2 and iodine to double bonds can take different pathways depending on the conditions employed. The reaction of silver nitrite and iodine in the presence of cyclohexene was reported as early as 1932 by Birchenbach et al. to yield dinitro and iodo-nitro adducts^[106a]. Only in 1964 was this reaction reinvestigated by Hassner and coworkers who emphasized its synthetic usefulness [63, 99, 107]. "In situ" nitryl iodide has been used also for the preparation of unsaturated nitro-sugars^[108].

[106] a) L. Birchenbach, J. Goubeau and E. Berniger, Ber. dtsh. chem. Ges. 65, 1339 (1932).

b) L. Birchenbach and J. Goubeau, ibid. 67, 1425 (1934).

[107] Presented before the Symposium on Electrophilic Additions to Olefins, 148th National Meeting of the ACS, Chicago, Sept. 1964, as cited in [63].

[108] W.A. Szarek, G.D. Lance and R.L. Beach, Chem. Comm. 1968, 356.

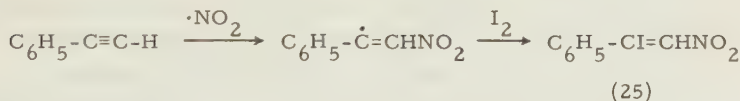
[109] G.B. Bachman and T.S. Logan, J. Org. Chem. 21, 1467 (1956).

Employing dinitrogen tetroxide - iodine leads to different products according to the addition sequence of the reactants. When an olefin is added to a N_2O_4 -iodine mixture, some iodoalkyl nitrate is formed along with the nitro-iodo adducts. This was shown by Bachman and Logan^[109] and later by Hassner^[99b]. Investigating the different reaction pathways, Hassner et al. had obtained nitroalkyl nitrates from olefins also with iodine nitrate prepared "in situ" from $AgNO_3$ and iodine, as mentioned earlier by Birchenbach and Goubeau^[106b].

The development of the most important method, giving high yields of iodo-nitro compounds almost exclusively, was initiated by a paper on the reaction of N_2O_4 and cyclohexene in the presence of bromo-trichloromethane^[96]. Brand and Stevens stated that all the products formed were derived from an intermediate β -nitroalkyl radical, which gave a complex reaction mixture containing some 30% of bromo-nitro compound^[96]. Stevens and Emmons then used iodine to trap this radical: N_2O_4 was passed in a slow stream of nitrogen into an ether solution of the unsaturated compound with excess iodine^[97]. Thus the nitroalkyl radical was generated in the presence of a large excess of iodine and unwanted side reactions were avoided. The dehydrohalogenation of the resulting nitroalkyl iodides leads to nitroolefins in high yield. This over-all process is the method of choice for the conversion of an olefin to a nitroolefin under mild conditions.

Stevens and Emmons also submitted acetylenes - toluene and phenylacetylene - to this reaction. From toluene 81% of a stereoisomeric mixture of the iodo-nitroolefin adducts were formed. Phenylacetylene was reported to give in 86% yield one of the two possible 2-iodo-2-phenyl-1-nitroethylene isomers (25) exclusively. From the UV spectrum the cis structure (with phenyl and NO_2 trans) was tentatively

assigned^[110], see fig.11, p. 69, cp. also the different conclusions out of this work in B-I/4.



The experimental control of this reaction as first crop gave 42% of the compound (25) whose melting point was in agreement with [97]. No attempt was made to increase the yield though the mother liquor still contained considerable quantities of (25).

To extend the NO_2 -iodine reaction of unsaturated compounds to alkyl-acetylenes, the above procedure had to be slightly changed. The alkyl-acetylenes employed here are much more volatile than phenyl-acetylene. Furthermore, their reactivity towards these additions is lower. This has already been stated in the reaction of nitryl chloride with phenyl- and tert-butylacetylene, resp.. Thus the reaction of N_2O_4 -iodine with alkylacetylenes $\text{R}-\text{C}\equiv\text{C}-\text{H}$ (R = tert-butyl, iso-propyl, n-butyl, n-propyl and iso-propenyl) was carried out with an acetone-Dry Ice reflux condenser and the reaction kept at about 0° during the introduction of N_2O_4 by a slow nitrogen stream (0.5-1 g N_2O_4 per hour). Following that, the reaction flask was allowed to warm up to room temperature, but the reflux condenser was left for one or two more days. Yields and ratio of the stereo-isomeric 2-iodo-1-nitroolefins prepared by this method are listed in the following table.

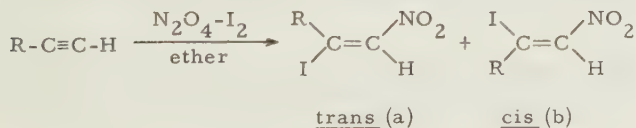


Table 2. Yield and Product Ratio from N_2O_4 -Iodine
Addition to Alkylacetylenes $R-C\equiv C-H$.

R	Addition products trans (a):cis (b)	GLC leaving temperature	Yield in %	Purity of Employed Ether
$C(CH_3)_3$	(26) 18 : 82	154°, 171°	85.3	dry (Mallinckrodt) > 99.9%
$CH(CH_3)_2$	(27) 62 : 38	146°, 161°	86.0	"
$n-C_4H_9$	(28) 75 : 25	171°, 182°	90.0	"
$n-C_3H_7$	(29) 78 : 22	156°, 170°	57.0	p.a. (UCB) > 99.5%

The purity of the employed ether was important for the yield of addition products: ether p.a. (Union Chimique Belge) usually gave a 30% lower yield than highly dried ether as seen in the case of $R = n-C_3H_7$ in table 2. The (a):(b) ratio was not affected by this as has been checked in the preparation of (26).

The separation of isomers (a) and (b) is based on their differing polarity. As seen from the gas_chromatographic data, the two isomers were well separated under standard conditions (see Experimental Section). On the preparative scale, however, decomposition to a large extent was observed. The separations finally were carried out successfully by LSC. Analytical amounts of the isomers (a) and (b) showed sufficiently different R_F values on chromatographic plates (silicagel, CCl_4). Again the trans isomer (a), more volatile according to GLC, passed faster due to its lower polarity.

[110] J.P. Freeman and T.E. Stevens, J. org. Chem. 23, 136 (1958).

Preparative separation here was accompanied by less decomposition: 70-80% of the starting material could be recovered. The different isomers showed purities from 90 to 100% (GLC and NMR control) as represented in table 2. The less volatile cis isomer (26b) could be obtained in pure state also by repeated precipitations from n-pentane at -80 to -60°. In the isopropyl compound mixture (27) the preponderant trans isomer was a solid, melting point 41-42°. Its purification therefore was accomplished also by recrystallization from n-pentane at -10° to 0°.

Mixtures and pure isomers of these 2-iodo-1-nitroolefins were stable when kept in the dark at 0°, otherwise the yellow liquids turned brown due to liberation of iodine. Addition of some mercury, dispersed by vigorous shaking, proved to be efficient to keep the liquids clear yellow.

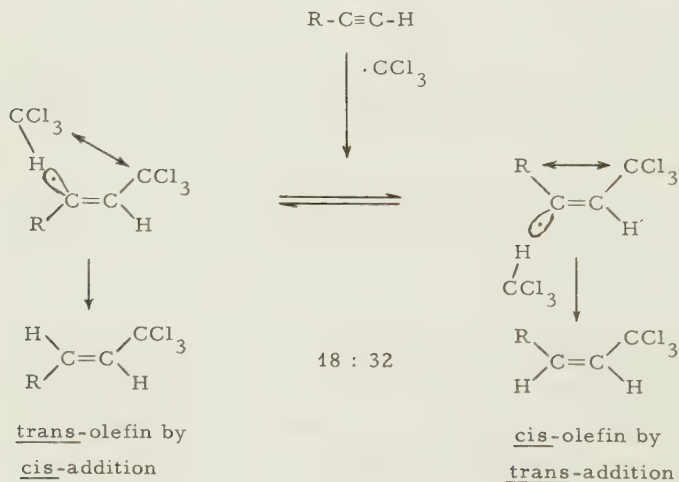
Several efforts were made to find out if the (a):(b) ratio corresponded to a thermodynamical equilibrium. A CCl_4 solution of iodine and the isopropyl isomer (27a) was kept at room temperature, but after several weeks no isomerization could be observed. Likewise solutions of (27a) in CCl_4 and ether, resp., were treated with N_2O_4 for several days, but no change could be detected.

Unfortunately, the stereochemistry of radical additions to acetylenes (or: the stereochemistry of vinyl radicals) has not yet been investigated systematically^[111]. Mostly one type of reaction has been studied with one alkyl- and phenylacetylene as substrates. However, there

[111] Compare M. Julia in loc. cit. [8b], Chapter 5 (Free Radical Additions to Acetylenes).

almost certainly different mechanisms and different hybridizations of the vinyl radicals are involved.

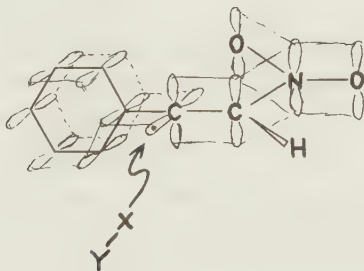
Kopchik and Kampmeier reported on the benzoyl peroxide catalyzed addition of chloroform to 1-hexyne^[112]. They obtained a kinetically controlled mixture of geometric isomers with 82:18 trans:cis addition. This was explained in terms of isomeric vinyl radical intermediates which interconvert rapidly with respect to subsequent reactions^[112]. The product ratio has been described to be due to the easy accessibility of the cis-radical for the hydrogen donor molecule (here CHCl_3). In other words, the interaction $\text{R} \leftrightarrow \text{CCl}_3$ is less important in this case than the interaction $\text{Cl}_3\text{C-H} \leftrightarrow \text{CCl}_3$. With smaller donors, subsequently, the formation of trans-olefins is favoured^[112].



[112] R.M. Kopchik and J.A. Kampmeier, J. Amer. Chem. Soc. 90, 6723 (1968).

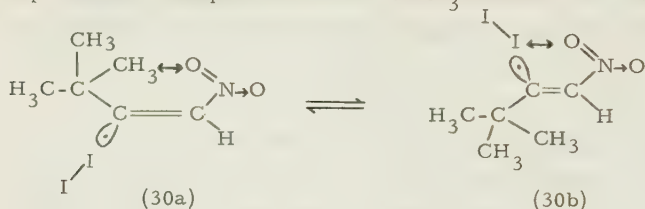
Kopchick and Kampmeier also give an explanation why the product ratio derived from vinyl radicals with an α -phenyl group does not fit to the above model. The enhanced reactivity of 1-phenyl-vinyl vs. 1-alkyl-vinyl radicals has been rationalized by an sp-hybridized resonance stabilized radical.

Considering these facts and hypotheses, the results of NO_2Cl and NO_2 -iodine addition to acetylenes can be understood. Phenylacetylene forms with both NO_2Cl and NO_2 -iodine almost exclusively the trans-isomer^[97, 105], that is addition of NO_2 and X in a trans manner. From a model of the intermediate 1-phenyl-2-nitrovinyl radical it is seen quite clear that the trapping of this radical is more favourable when NO_2Cl or an iodine molecule approach from the rear side of the nitro group :



This rough picture is supported by the results of the NOCl -phenylacetylene^[105] and the N_2O_4 ^[49] or NO_2 -iodine^[97] - toluene addition reactions. As expected, the linear NO group attached to the C-C system in the first step, hinders less the approach of further NOCl as Cl donor than does the nitro group. The amount of product deriving from cis-addition increases to 15% vs. traces found from the analogous reaction with NO_2Cl ^[105].

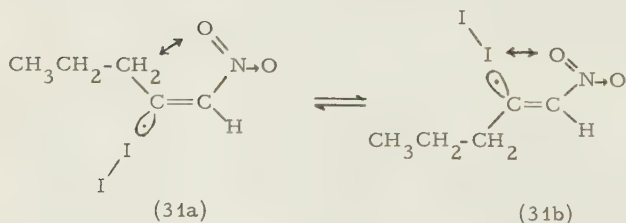
The addition of NO_2 -iodine to alkylacetylenes may be rationalized considering interactions $\text{R} \leftrightarrow \text{NO}_2$ and iodine $\leftrightarrow \text{NO}_2$ as discussed by Kopchick and Kampmeier for the CHCl_3 addition to 1-hexyne^[112].



(26), 18:82

2-iodo-1-nitroolefin

(29), 78:22

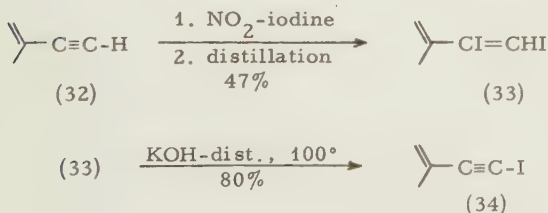


In the tert-butyl case the isomer (30b) of the rapidly interconverting radical pair should be much more favoured than (30a), but the iodine approach to (30b) is more difficult. According to the 18:82 product ratio observed the effect of steric crowding due to cis-tert-butyl and nitro group is predominant. This ratio 18:82 changes to 78:22 when tert-butyl is replaced by n-propyl. In the respective radical pair equilibrium the trans isomer (31b) is still favoured, but less than in the tert-butyl case. At the same time the iodine- NO_2 interaction of (31b) remains considerable as in the case of (30b). Furthermore, the iodine approach to (31a) is about as favourable as for (30a). The

result of these two main effects $n\text{-C}_3\text{H}_7 \leftrightarrow \text{NO}_2$ in (31a) and $\text{I-I} \leftrightarrow \text{NO}_2$ in (31b) is the preponderant formation of the trans-addition product from (31a). Thus the product ratio 78:22 is mainly determined by the unfavourable I_2 approach to (31b). The influence of the solvent ether with respect to stabilization or destabilization of the above radicals, however, is not known.

The reaction of NO_2 -iodine with isopropenylacetylene (32) took a different course. During the addition of NO_2 an ochre precipitate was formed that contained nitro groups according to the IR spectrum. Most likely, this material was polymeric, because it was insoluble in common organic solvents. Elemental analysis showed that two molecules of the acetylene (32) had taken up one nitro group and 0.6 iodine atoms.

The solution was worked up as usual to give a dark brown oil that showed nitro group absorptions in the IR spectrum. The volatile material, however, contained no longer nitro groups. It consisted of an isomeric mixture of pure 1,2-diiodo-3-methyl-1,3-butadiene (33), a dark red-brown mobile liquid that decomposed within a few days at room temperature. When (33) was distilled through a KOH-packed tube, as described for the preparation of tert-butylnitroacetylene (section B-II), one mole of HI was removed. The resulting 1-iodo-3-methyl-3-buten-1-yne (34) was a pale-yellow liquid, which decomposed also very readily.



The formation of (34) by this method is unusual for the preparation of an iodoacetylene^[9]. Mostly substitution methods are applied for their synthesis^[9]. (34) has not yet been described in the literature^[9]. Its structure is established by its analytical and spectral data. In the IR spectrum of (34) (Fig. 7) the $C\equiv C$, $=CH_2$, and $C-CH_3$ units are recognized easily:

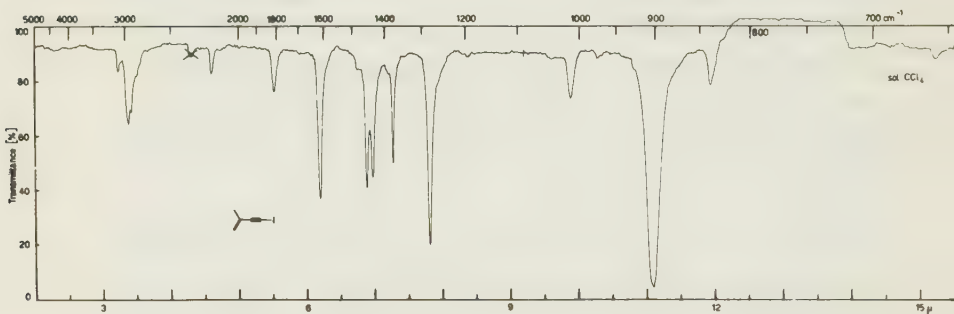
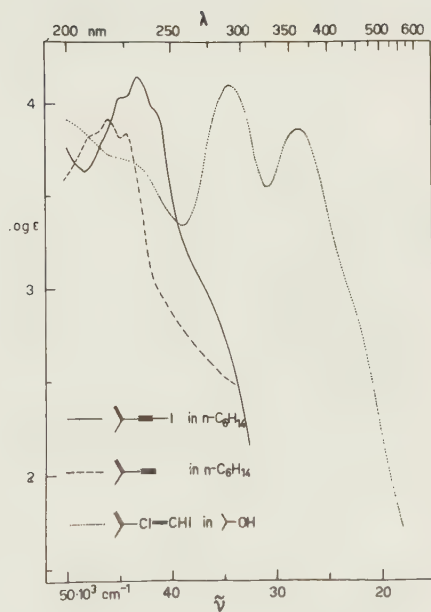


Fig. 7. IR Spectrum of Isopropenyl-iodoacetylene (34).

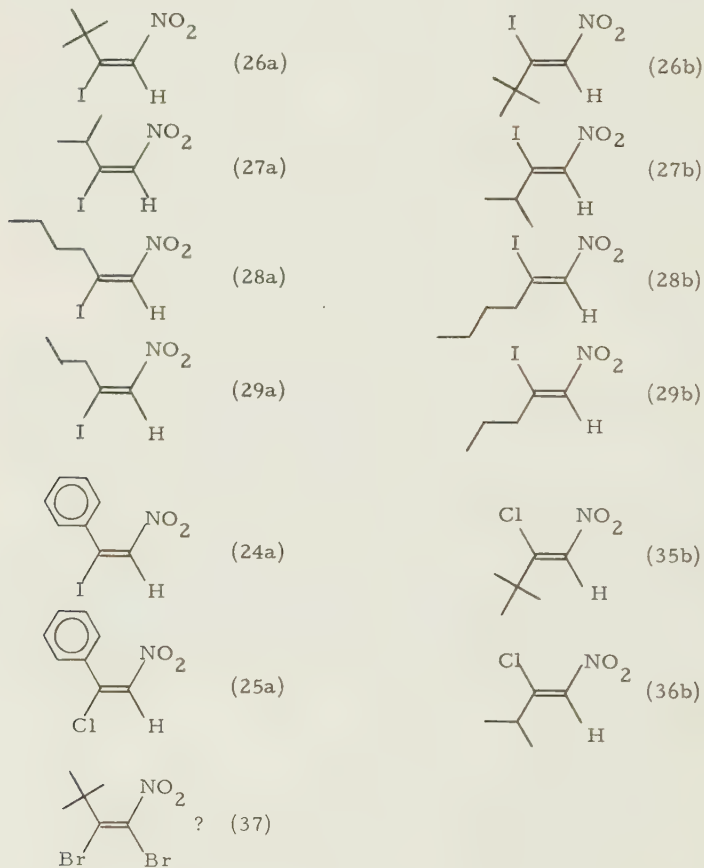
The UV spectrum of (34) demonstrates its relationship to the starting compound, isopropenylacetylene, which is seen in fig. 8. The spectrum of the diiodobutadiene (33) is completely different.

Fig. 8. UV spectra of
(32), (33), (34).



4. Configuration of 2-halo-1-nitroolefins^[*]

The following 2-halo-1-nitroolefins have been prepared in the course of this work:



[*] cis, trans : with respect to the sequence of atomic weights of the substituent atoms.

The alkyl-iodonitroolefins (26)-(29) were always obtained as an isomeric mixture. Their configuration can be assigned to by:

- a) GLC and LSC migration rates,
- b) NMR spectra,
- c) UV spectra,
- d) IR spectra.

a) During the work on nitropropene isomers the relative GLC retention times of trans- and cis-1-nitro-1-propene were found to be 1.00 and 0.74, resp.^[19a]. This was explained by the different shape of the molecules that cause lower polarity and thus higher volatility of the cis-isomer. Similarly, the trans-2-iodo compounds are considered to be less volatile than their cis isomers. The C-C=C-NO₂ chain remains the same here as in the above nitropropenes. Introduction of iodine is not expected to change the relative volatilities (or polarities) decisively. Indirect evidence also comes from the increasing content of the more volatile isomer: when tert-butyl is replaced by the isopropyl group, the product ratio changes from 18:82 to 62:38 (see B-I/3a). This must be rationalized by a decrease of steric hindrance, which is relevant only in the trans isomers, that is with alkyl and nitro group cis. Thus to the compounds of the "a series", which show smaller GC retention times and higher R_F values, the trans structure (NO₂ and iodine trans) is assigned.

b) In nitropropenes as model compounds the chemical shifts of the methyl groups are influenced by the nitro group similar to the olefinic protons^[19a, 79], but to a lesser extent^[19a]. Compared to the propene methyl group^[113], the nitro substituent shifts a

^[113] A.A. Bothner-By and C. Naar-Colin, J. Amer. Chem. Soc., 83, 231 (1961).

geminal $\text{CH}_3 > \text{cis-CH}_3 > \text{trans-CH}_3$ downfield. From a series of methyl-substituted nitroolefins^[49, 79] the following values result:

$$\text{NO}_2 \text{ gem. } 0.50, \text{ NO}_2 \text{ cis } 0.40, \text{ NO}_2 \text{ trans } 0.26 \text{ ppm.}$$

A similar influence of the nitro group is stated for allylic methylene or methine protons.

The n-butyl and n-propyl derivatives (28) and (29), resp., show allylic CH_2 peaks at ≈ 3.15 ppm for the more volatile isomers (28a) and (29a) and ≈ 2.73 ppm for the other isomers. This is illustrated by the NMR spectrum of a mixture of (29a) and (29b) in fig. 9:

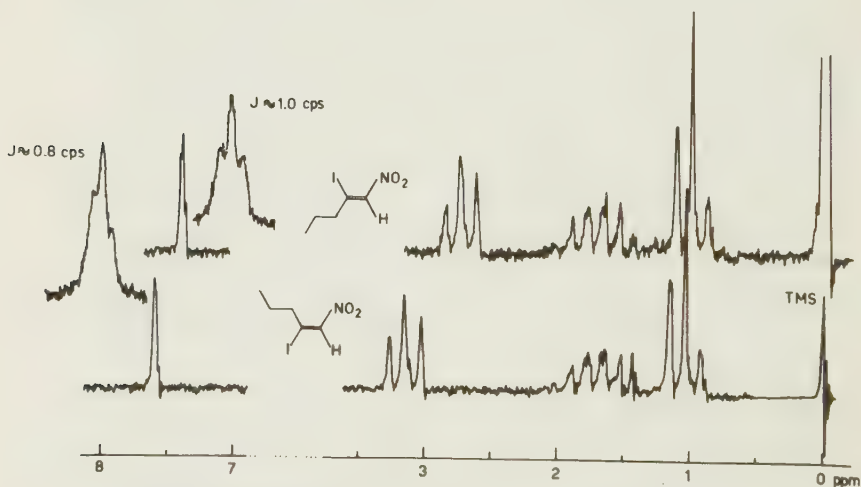


Fig. 9. NMR Spectrum of a Mixture of Stereoisomeric 2-Iodo-1-nitro-1-pentenenes (29a) and (29b).

In the NMR spectrum of the more volatile isopropyl compound (27a) the allylic tertiary proton appears at 3.39 vs. 2.55 ppm found for the other isomer (27b). Thus to the more volatile isomers of the "a series" must be assigned the trans structures. Therein NO₂ and alkyl groups are in cis position with respect to each other.

The positions of olefinic protons do not differ enough to determine the configurations of the above 2-iodo-1-nitroolefins unequivocally. The values are listed below (all obtained from CCl₄ solutions).

Compound	Isomer (a)	Isomer (b)
(26)	7.24	7.26
(27)	7.52	7.43
(28)	7.52	7.35
(29)	7.56	7.37

Besides the tert-butyl compounds, the olefinic proton of the (a) isomer always appears slightly more downfield than that of the (b) compound.

The preliminary iodine increments, calculated by Pascual et al. from only four compounds, were $Z_{cis} = 0.81$ and $Z_{trans} = 0.88$ ppm^[78b]. However, the values calculated from the above iodonitroolefins (27-29) are lower: $Z_{cis} = 0.60$ and $Z_{trans} = 0.40$ ppm.

c) Nitroolefins of the general formula R-CH=CH-NO₂ absorb at 225-230 nm in hydrocarbon solvents. Introduction of iodine in the 2-position gives rise to a bathochromic shift of ≈ 50 nm as seen from table 3 and fig.10. Only in one case significant differences in the UV absorption occur. In the UV spectrum of (26a), fig. 10, the main absorption band has disappeared, which reflects the

Table 3. Positions and log ϵ Values in the UV Spectra of Halonitroolefins,
Solvent n-Hexane.

Compound	Isomer (a) Alkyl-NO ₂ <u>cis</u>	Isomer (b) Alkyl-NO ₂ <u>trans</u>
$\text{H} \begin{array}{c} \diagup \\ \text{C}=\text{CHNO}_2 \\ \diagdown \end{array}$ (17d)		228.5 (4.02)
$\text{Cl} \begin{array}{c} \diagup \\ \text{C}=\text{CHNO}_2 \\ \diagdown \end{array}$ (35)		246 (3.80)
$\text{Cl} \begin{array}{c} \diagup \\ \text{C}=\text{CHNO}_2 \\ \diagdown \end{array}$ (36)		246 (3.84)
$\text{I} \begin{array}{c} \diagup \\ \text{C}=\text{CHNO}_2 \\ \diagdown \end{array}$ (26)	211.5(3.85) sh 250(3.22)	208 (3.70) 279 (3.46)
$\text{I} \begin{array}{c} \diagup \\ \text{C}=\text{CHNO}_2 \\ \diagdown \end{array}$ (27)	212 (3.53) 274(3.64)	210 (3.78) 279 (3.63)
$\text{I} \begin{array}{c} \diagup \\ \text{C}=\text{CHNO}_2 \\ \diagdown \end{array}$ (28)	sh 213 (3.67) 275(3.76)	212 (3.58) 279 (3.64)
$\text{I} \begin{array}{c} \diagup \\ \text{C}=\text{CHNO}_2 \\ \diagdown \end{array}$ (29)	sh 212 (3.70) 275(3.76)	210 (3.72) 279 (3.60)

Table 3 (contd.)

Compound	Isomer (a) Alkyl-NO ₂ <u>cis</u>	Isomer (b) Alkyl-NO ₂ <u>trans</u>
 (17c)		229 (3.99) 299 (4.25) [114a]
 (24)	223.5(3.98) sh 238.5(3.94) 277 (3.64) lit. [105]; 223 (4.00), 277 (3.68)	226.5 (3.91) 287 (4.07) [105]
 (25)	239.5(4.04) sh 280(3.81) lit. [110]; sh 244 (4.15) 284 (3.97) in EtOH	
 (15c)		229 (3.88) 313.5 (4.11) [114b]
 (15d)		213 (3.60) 263 (3.60)
 (37)	212 (4.12) sh 235(3.3)	284 (2.53) sh 340 (2.0)

destruction of coplanarity by steric interference of cis tert-butyl and nitro groups. Apparently no other explanation is possible. When passing from the tert-butyl compound (26) to the n-propyl derivative (29) of the "a series", the isopropyl derivative (27a) already behaves quite normal compared with the least strained n-alkyl isomer (29a), see fig. 10. The compounds (b) with iodine and nitro substituents cis absorb at slightly higher wavelengths than their stereoisomers (a): throughout the whole series 279 vs. 274-5 nm is found, see table 3 and fig. 10.

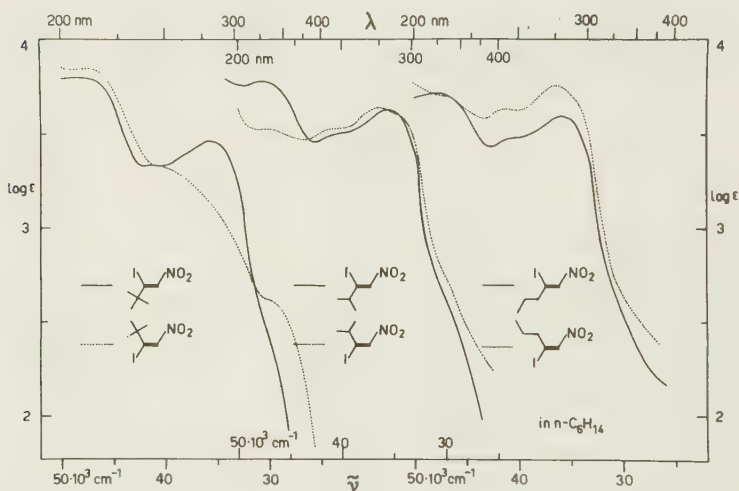


Fig. 10. UV Spectra of the Stereoisomeric 2-Iodo-1-nitroolefins (26), (27), (29).

- [114] a) E.A. Braude, E.R.H. Jones and G.G. Rose, J. Chem. Soc. (London) 1947, 1104.

b) For the UV spectrum of (15c) in ethanol cp. [114a].

- [115] a) J.F. Brown Jr., J. Amer. Chem. Soc., 77, 6341 (1955).

b) C.N.R. Rao in H. Feuer (ed.), "The Chemistry of the Nitro and Nitroso Groups", Pt. I, Chapter 2 (Spectroscopy of the Nitro Group), Interscience 1969.

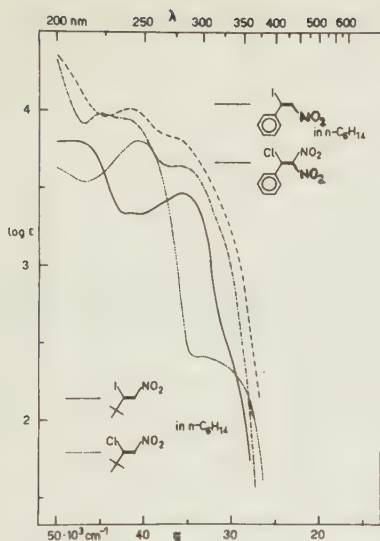


Fig. 11. UV Spectra of 2-Chloro-1-nitroolefins (24a), (35b) and of 2-iodo-1-nitroolefins (25a) and (26b).

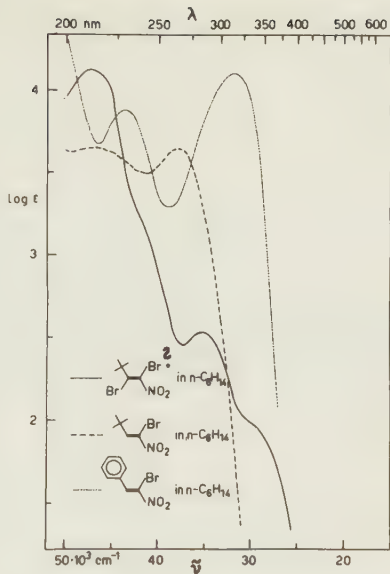


Fig. 12. UV Spectra of the Bromo-nitroolefins (15c), (15d) and (37).

d) The IR spectra of the 2-iodo-1-nitroolefins (26), (27) and (29) are given in figs. 13 and 15 on the next pages. Comparing the positions and intensities of the C=C stretching absorptions, it is again the more volatile of the tert-butyl derivatives, (26a), which is exceptional. Its double bond absorption occurs at 1647 cm^{-1} , whereas the other 2-iodo-1-nitroolefins absorb in the range $1610\text{--}1595\text{ cm}^{-1}$. All the asymmetric stretching vibrations appear between $1524\text{--}1540\text{ cm}^{-1}$, the symmetric stretching modes at $1335\text{--}1348\text{ cm}^{-1}$. In (26a) the latter vibration absorbs as high as 1370 cm^{-1} which is already in the range of saturated nitro compounds^[115].

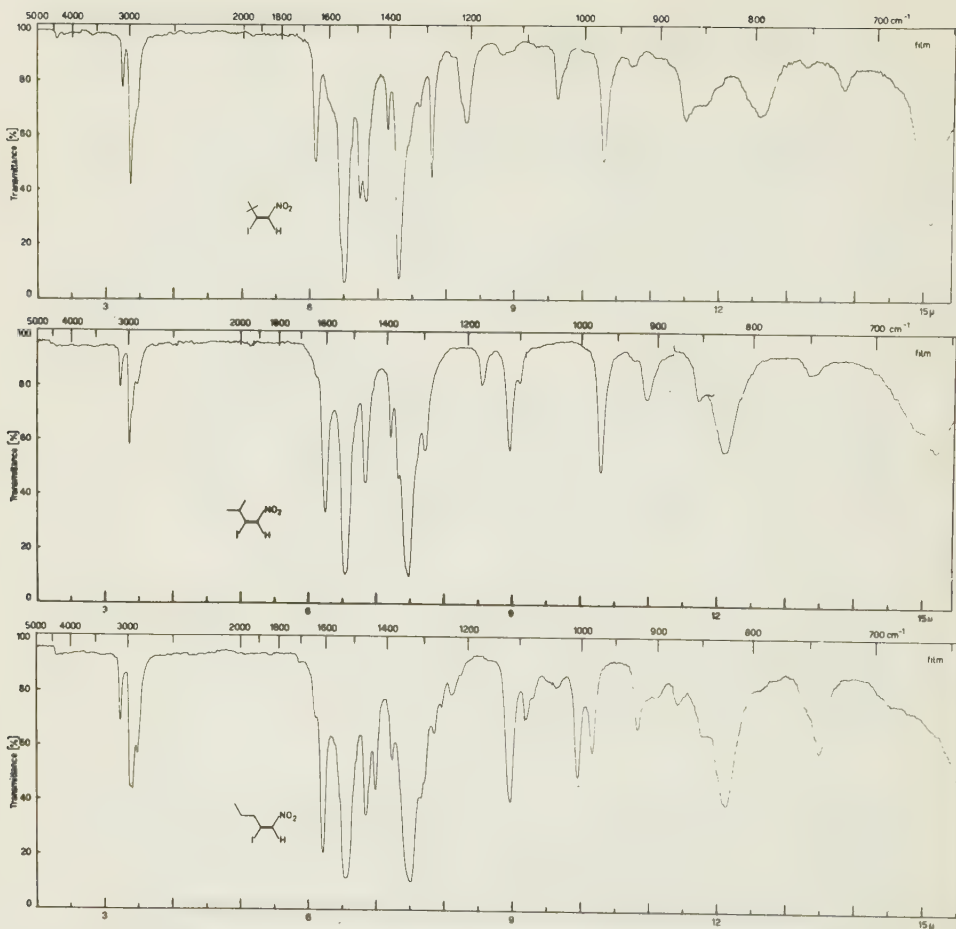


Fig. 13. IR spectra of trans-2-iodo-1-nitroolefins (26a), (27a), (29a).

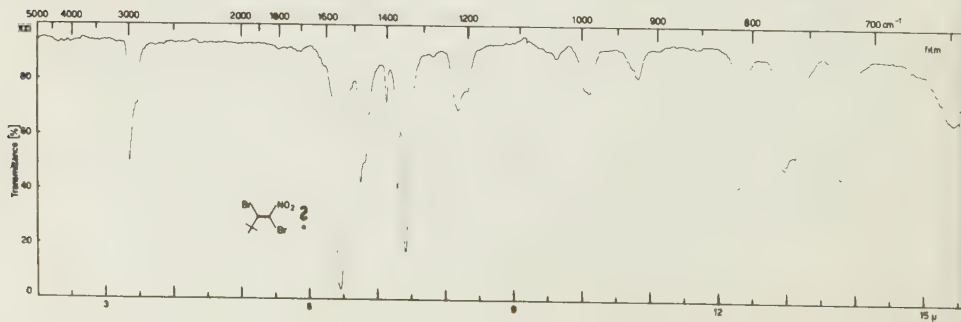


Fig. 14. IR spectrum of the 1,2-dibromo-1-nitroolefin (37).

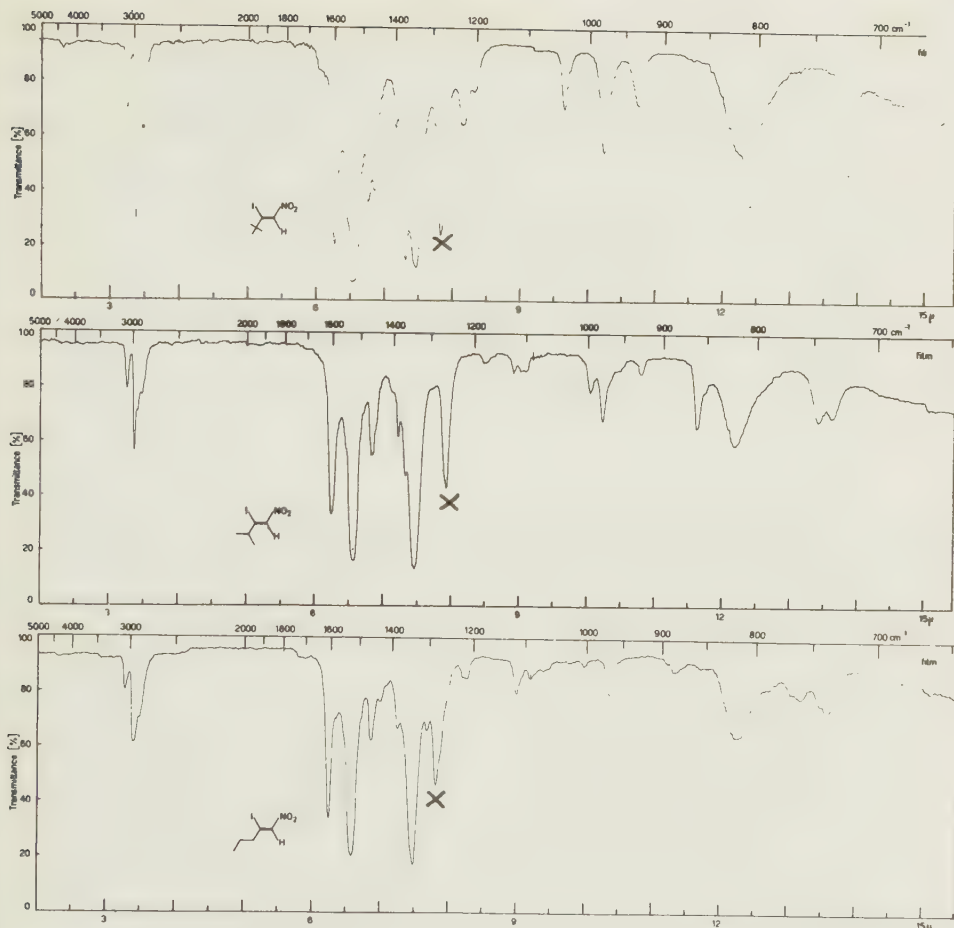


Fig. 15. IR spectra of *cis*-2-iodo-1-nitroolefins (26b), (27b), (29b).

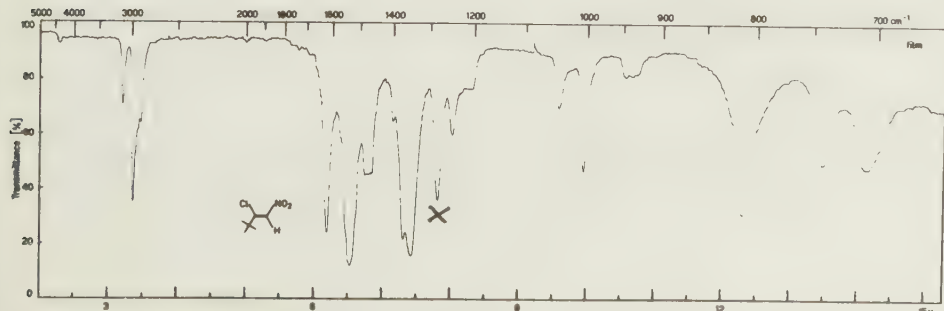


Fig. 16. IR spectrum of the *cis*-2-chloro-1-nitroolefin (35b).

The C-H valence vibrations of the olefinic hydrogen do not allow to distinguish between the two series of isomers. However, a medium strong band at $1275 \pm 8 \text{ cm}^{-1}$ is found in all compounds of the "b series". In the "a series" this absorption band is absent or, in the IR spectrum of (26a), of a different shape and lower intensity. The 1275 cm^{-1} band is marked by a cross on the spectra in fig. 15. This characteristic band cannot be assigned with certainty. Tert-butyl skeletal vibrations in hydrocarbons occur at 1250 ± 5 and $1250\text{-}1200 \text{ cm}^{-1}$ [42, 116], but the above 1275 cm^{-1} band may derive from an unusually shifted C-H deformation mode as well.

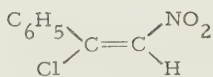
The configurations of 2-alkyl-2-iodo-1-nitroolefins thus have been established by a variety of consistent findings from four different methods. The results shall now be applied to the spectral data of other 2-halo-1-nitroolefins, where only one isomer has been isolated.

That the 2-chloro-1-nitroolefins (35) and (36) (their synthesis is discussed in B-IV/5) belong to the "b series", is shown unambiguously by their NMR, UV and IR spectra. Comparison of the estimated chemical shifts of the olefinic protons with the observed values gives no hint, because the values for the (a) and (b) isomers are too close. The position of 2.7 ppm for the allylic proton in the isopropyl-chloronitroolefin (36), however, fits closely the value of the corresponding iodo derivative (27b), which is 2.55 ppm. In the trans-iodonitro compound (27a) a value of 3.39 ppm has been found, see p. 65.

[116] L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules", Methuen-Wiley, London-New York, 2nd ed., 1966.

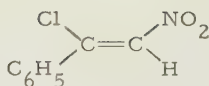
The UV spectrum of the tert-butyl compound (35) exhibits a $\lambda_{\text{max}} = 246 \text{ nm}$ ($\log \epsilon \text{ } 3.80$). There is no suppression similar to that in the sterically hindered compound (26a) with tert-butyl and NO_2 cis (compare table 3 and figs. 10, 11). According to their IR spectra, (35) and (36) are also seen to be members of the "b series". This is concluded from the medium strong bands at 1282 and 1270 cm^{-1} resp., which have been shown to be characteristic for this configuration. Further, the pattern of the IR spectra of (35) and (36) in the entire range recorded, fits very closely those of the iodo analogs (26b) and (27b), but not those of (26a) and (27a). The IR spectrum of (35b) is given in fig. 16.

The phenyl derivatives (24) and (25), isolated during this work, have the same steric arrangement. This is proven by their closely related UV and IR spectra. Iwai and coworkers in 1965 had isolated both isomers of (24)^[105]. By comparison of their UV spectra with that of *o*-nitrostyrene they have shown that in the liquid isomer, obtained by the action of NOCl on phenylacetylene, phenyl and nitro group were trans. In the other solid isomer isolated from the NO_2Cl -phenylacetylene reaction (cp. B-I/2), the benzene ring and the nitro group are oriented at a considerable angle out of the plane of the ethylenic bond. The most remarkable consequence of this is that the intensity of the second absorption band in the UV spectrum of the solid isomer is reduced (see table 3 and lit.^[105]). To the iodo compound (25) erroneously the cis structure (phenyl and NO_2 trans) has been assigned^[97]. UV and IR spectra of (25) leave no doubt that it is the trans isomer belonging to the "a series". The structures (24a) and (25a) given are further supported by their NMR spectra. The positions of the olefinic protons in the two possible isomers of (24) and (25) were estimated from the increments of their respective substituents (iodine values see p. 65). The experimental values are in good accord with those calculated for the (a) isomers:



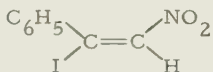
(24a)

$\delta_{\text{=H}}$ calc. 7.32
found (CCl₄) 7.42



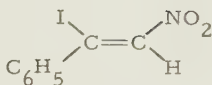
(24b)

7.70



(25a)

$\delta_{\text{=H}}$ calc. 7.74
found (CDCl₃) 7.62



(25b)

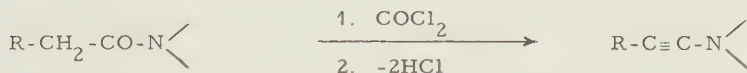
7.25

The structure of the dibromo adduct (37), prepared from tert-butyl nitroacetylene and bromine (see B-IV/3), cannot be proven unequivocally as no olefinic hydrogen is present. In its IR spectrum (fig. 14) the C=C stretching mode is absent or swamped by the very strong asymmetric NO₂ band which appears unusually high at 1550 cm⁻¹. In the UV spectrum of (37), represented in table 3 and fig. 12, no maximum comparable with those in 1-bromo-1-nitroolefins (15) appears. One might tend to attribute the configuration with the tert-butyl and nitro group cis because of the similarity of its UV spectrum with that of (26a). However, this would implicate cis addition of bromine to the triple bond of tert-butyl nitroacetylene. The problem presented here may be rationalized when the corresponding i-propyl and n-propyl compounds are accessible.

II. Synthesis of Nitroacetylenes.

1. Preliminary attempts from 2-halo-1-nitroolefins.

When this work on the synthesis of nitroacetylenes was started, first the preparation of electronically substituted derivatives, i. e. nitroynamines, was envisaged. One of the methods to synthesize ynamines starts with substituted acetamides, which on treatment with phosgene are first converted to amide chlorides. Twofold HCl elimination then leads to ynamines^[8].



Similarly, in our nitroynamine project nitroacetamides were the starting material. Difficulties in the preparation of these barely known substances could be overcome, but the nitroacetamides were inert towards phosgene. N,N-diethyl dichloroacetamide, also unaffected by phosgene, was chosen as a model compound to study the oxygen-chlorine exchange. Pyrocatechyl phosphorous trichloride proved reactive in converting this amide directly into the dehydrochlorinated product, a trichlorovinylamine^[117]. Preliminary tests with this reagent on nitroacetamides looked promising. Nevertheless, these attempts had to be abandoned. Eliminating hydrogen iodide from 2-iodo-1-nitroolefins - a project followed simultaneously - had made the sterically stabilized first authentic nitroacetylene derivative, tert-butylnitroacetylene, easily accessible^[1]. Consequently our work concentrated on this preparative method and the reactions of the nitroacetylenes obtained thereby.

Of the series of 2-halo-1-nitroolefins, HX elimination was tried first from the phenyl derivatives. Indeed triethylamine in solution or in the pure state

[117] V. Jäger and H. G. Viehe, unpublished results 1968.

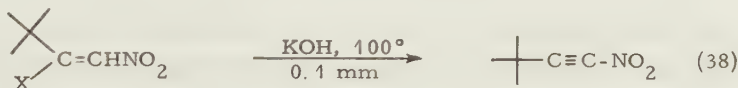
gave a precipitate of ammonium chloride. However, IR spectroscopic control of the dark-red solutions showed, besides large amounts of unchanged starting material, no absorption in the triple bond region. Trapping experiments with triethylamine as base and furan or tetracyclone as trapping agents failed. Likewise, treatment of the phenyl derivatives (24a) and (25a) with potassium tert-butoxide, sodium acetate in DMF and Ag_2O in refluxing ether met with no success. Distillation of the chloro-derivative (24a) from mixtures with sodium acetate or Ag_2O at 100° under reduced pressure gave only starting material. The tert-butyl derivative (2b) behaved similarly in eliminating HI on treatment with triethylamine. The eliminations in solutions of (2b) in triethylamine and ethyl-di-iso-propylamine were followed by IR spectroscopy. Very small absorptions at $\approx 2250 \text{ cm}^{-1}$ with 95% transmission instead of 100% in the starting product were the best results.

2. HX eliminations from 2-halo-1-nitroolefins to nitroacetylenes.

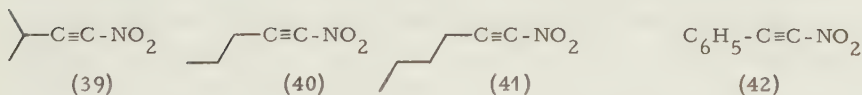
During the preceding work on nitroolefins^[19a, e, f ; 118] at the University of Erlangen it was found that polymerization and possible explosive decompositions in the synthesis of nitropropenes from β -nitroalkyl acetates could be avoided by carrying out the elimination the following way : these preparations were run in a heterogeneous manner so as to exclude polymerization of the nitroolefins. Powdered sodium acetate was used as elimination catalyst and diphenylether at $100\text{--}110^\circ$ as reaction medium. Secondly, the reaction system was kept under vacuum, so that the elimination products were distilled off immediately after formation. After the negative results of 1-bromo- and 2-iodonitroolefins with bases such as amines in solution (see A-I/4, 3 ; A-II/3 and

^[118] G. Hesse and V. Jäger, Liebigs Ann. Chem., in press.

preceding paragraph) a similar procedure was thought to be effective for the synthesis of base- and temperature-sensitive nitroacetylenes. Thus, when the isomeric mixture of tert-butyl derivatives (26) was distilled in preliminary tests through a KOH-packed tube of 20 cm length heated to 110-120°, the IR spectrum of the distilled products for the first time showed a substantial amount (ca. 30%) of nitroacetylene. This could be judged from the very intense split absorption bands at 2 230 and 2 270 cm⁻¹. Slight changes of the distillation apparatus, heating system and distillation rate gave an optimum yield of 96-97% of nitroacetylene (38), GLC purity 98-100% :



(26), X=I ; (35b), X=Cl.



If the distillation rate (ca. 1 g per hour) or the elimination temperature were not properly adjusted as to afford nitroacetylene (38) along with some starting material, redistillation through a KOH tube under the same conditions gave pure material. The elimination of HCl from the cis-chloro derivative (35b) - prepared by the action of dry hydrogen chloride on (38), see B-IV/5 - proceeded equally well as verified in one run. The preparation of iso-propylnitroacetylene (39) was achieved similarly though it proved more delicate because of the lower stability of this sterically less protected

nitroacetylene under these conditions. Here the increasing ease of decomposition afforded lower elimination temperatures of 86-88°. Therefore the elimination process was less efficient and the distillation had to be carried out more slowly, about 0.3-0.5 g vs. ca. 1g/hour with the tert-butyl compound (26). In spite of this, the elimination usually was not complete and variable amounts of starting material were also trapped. For purification, all the material was redistilled at 0-10°/0.1 mm in bulb tubes and collected at -78°. Nevertheless, the yield of nitroacetylene (39) reached 74-76% (97% pure according to NMR).

Whereas during the preparation of (39) under optimal conditions the KOH pellets turned slightly red-brown, in the distillation of the n-propyl derivative (29) it turned dark-brown or even black thus indicating decomposition to a large extent. The elimination temperature had to be decreased further to 81-83°. The collected material contained about 50% starting material and was redistilled as above. The maximum yield of n-propylnitroacetylene (40) was 28%, purity of this material 90% (NMR).

Likewise, the preparation of n-butylnitroacetylene (41) proved to be a very subtle process. (41) was obtained along with starting material and was not purified further. Its properties and IR spectral data resembled those of (40). When the phenyl-chloro compound (24a) was distilled as above, a mixture of phenylnitroacetylene (42) along with starting product was also obtained. The existence of (42) was proven by IR spectroscopy. However, it was at the same time too unstable and not sufficiently volatile for further purification.

The crucial problem in the synthesis of sterically less protected nitroacetylenes such as (39)-(42), according to the above procedure, was always to optimize the elimination temperature and distillation rate. Higher temperatures 95-100° gave smooth elimination, but at the same time the decomposition of these nitroacetylenes increased. When the elimination temperature was too high, the decomposition of the nitroacetylene was indicated by the brown or even black colour of the KOH pellets' surface. At lower temperatures the elimination was incomplete and unchanged starting material passed. This could be overcome in part at the preparation of (39) and (40) on distilling the starting products very slowly, but less for (41) and (42). An easy check of the success of an elimination attempt was always the presence or absence of the strong lachrymatory odour of nitroacetylenes in the distilled product.

The eliminations from iodo-nitroolefins described above were achieved from stereoisomeric mixtures. In two experiments the pure cis-isomers (26b) and (35b) were employed, but tert-butyl nitroacetylene (38) formed by trans elimination was isolated in the usual yield. The dehydrohalogenation of olefins by trans elimination in general is highly favoured. However, the $k_{\text{trans}}/k_{\text{cis}}$ ratio diminishes when olefins with strong electron-withdrawing substituents are present, as it is the case in our nitro derivatives. Similar results have been reported when more powerful bases are applied^[24]. Thus we meet both levelling effects in the eliminations to nitroacetylenes reported here, and k_{trans} and k_{cis} obviously are of the same order of magnitude.

III. Properties of Nitroacetylenes.

1. General.

The three nitroacetylenes (38)-(40) isolated were slightly yellowish green liquids with a strong, lachrymatory odour similar to the lower members in the nitroolefin series. They all could be distilled at 0-10° under 0.1 mm pressure. The tert-butyl derivative had a relatively high melting point of about -3°, where it formed nearly colourless crystals; it distilled with partial decomposition at $\approx 55^\circ/15 \text{ mm}$.

Compared with molecules of similar high ground state energy as fluoroacetylenes^[9], a surprising thermal stability was stated. For example, the tert-butyl derivative (38) in one attempt was purified by preparative GLC, where still some 10% passed undecomposed. Gas_chromatograms of analytical tert-butyl-nitroacetylene quantities showed no decomposition under standard conditions (see Experimental Section), compared with the perfectly stable tert-butylnitroethylene. The iso-propyl derivative (39), however, showed already 30-50% decomposition. From a sample of the n-propyl compound (40) only 10-20% passed unchanged when an analytical sample was injected.

The decomposition of (38) at room temperature was followed by GLC and IR spectroscopic control. The half-life was found to be at least 2-3 days; this value was quite sensitive to the presence of basic impurities. The corresponding values for (39) and (40) were not determined exactly, according to rough estimates their half-life should be about 10 and 1-2 hours, resp., at room temperature.

Heating pure (38) in an IR cell left about 50% undecomposed material after half an hour, according to the decrease of the triple bond absorption. When a 20% solution of (38) in toluene was kept at 80-85°, again after 0.5 hours about 50% of the starting material had decomposed, after 10 hours only a few percent of (38) were still present. A sample of tert-butylnitroacetylene (38) heated on a water bath decomposed slowly, but not explosive. As in other cases the liquid turned orange-yellow and after two hours at 100° only a trace of the starting material had survived (IR). In spite of this thermal instability it has been shown, however, that tert-butyl-nitroacetylene is sufficiently stable in dilute solutions of non-polar solvents as to carry out reactions at temperatures up to 110-120°^[119].

Some qualitative tests were made also to get information about the dangers involved in working with nitroacetylenes, especially with (38). With nitroolefins as nitropropenes, nitroethylene and others on distillation sometimes explosions have been encountered^[19, 22b]. Overheating small quantities of (38) in a test tube or dropping (38) on a glowing iron nail did not lead to explosions. Pop decompositions of (38) were achieved, nevertheless, when pure (38) was treated with undiluted amines such as secondary amines, enamines or ynamines. One drop of these bases given to 100 mg quantities of (38) in a test tube made the mixture heat up and mostly bursting into flame.

The surprising oligomerizations of tert-butylfluoroacetylene^[9, 14] to valence isomers of benzene and some tetrameric material raised the question if similar oligomers were formed on the decomposition of tert-butylnitroacetylene. The disappointing result of the decomposition of (38) after standing for one month at room temperature shall be illustrated by the NMR spectrum of the final liquid product (fig. 17):

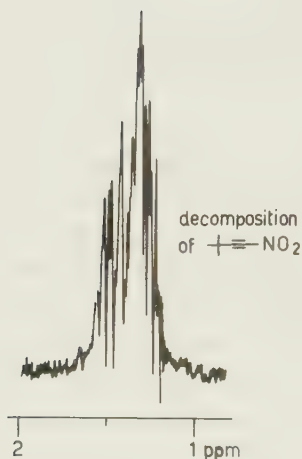


Fig. 17. NMR Spectrum of Decomposed tert-Butyl-nitroacetylene (38).

More than 18 tert-butyl peaks were present according to the above spectrum. GLC showed at least 20 different volatile compounds, one of them unchanged (38). In the IR spectrum the strong absorption bands of the nitro groups were still present, from the UV spectrum it seemed that no unsaturated nitro group unit had remained intact (fig. 18, p.85). Elemental analysis confirmed that (38) had transformed without substantial loss of volatile fragments as NO, NO₂: it deviated only slightly from that of the starting product. The maximum difference was a N value of 8.97% instead of 11.02% for (38). The average value for the molecular weight of this mixture was found to be 265 vs. 127 for (38). On the TL plate one very long spot was found indicating no separation under these conditions. A similar tail was observed when the product after LAH reduction and benzoxylation was submitted to TLC.

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- [119] a) J.-C. Motte, Mémoire de Licence, Univ. Louvain, 1970.
 b) A. Lecoq, Mémoire de Licence, Univ. Louvain 1970.

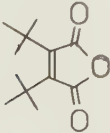
As at the decomposition of (38) at 100° or at room temperature some colourless crystals precipitated, there was at least one decomposition product that could be isolated (1% yield). The structure of this compound could not be established. Elemental analysis and molecular weight fitted the formula $C_{12}H_{18}N_4O_8$ suggesting its formation from two molecules of (38) plus two NO_2 :



IR and UV spectra (fig. 18, p. 85) permitted no assignment of the structure. Only from the NMR spectrum (1 peak) was it learnt that the two tert-butyl groups should be identical, thus proposing a symmetric molecule. The structure of this curious compound will be determined by X-ray analysis^[120].

2. Spectral data of nitroacetylenes.

The NMR spectra of the nitroacetylenes prepared are rather simple in showing peaks expected of the corresponding alkyl substituents. (38) gave rise to a single peak at 1.34 ppm in CCl_4 . This is quite downfield compared to other tert-butyl groups attached to aliphatic carbon atoms (all in CCl_4) and reflects once again the electro-negativity of the nitro substituent:

$Me_3C-CH=CH_2$	1.00 ^[121]	$Me_3C-C\equiv C-H$	1.20 ^[123]
$Me_3C-CH=CH-NO_2$	1.15 ^[72]	$Me_3C-C\equiv C-NO_2$	1.34 ^[1]
	1.49 ^[122]	$Me_3C-C\equiv C-COOEt$	1.32 ^[122]
		$Me_3C-C\equiv C-CN$	1.32 ^[122]

An unusual large solvent shift^[122] of -0.59 to 0.75 ppm is observed when the spectrum is taken in D₆-benzene.

The UV spectra of the nitroacetylenes (38)-(42) resemble those of the trans-1-nitroolefins (17), as to be expected. Maxima and ϵ values are listed in table 4.

Table 4. UV Absorptions of Nitroacetylenes (38)-(40) and Corresponding Nitroolefins.

Compound	$\lambda_1(\pi \rightarrow \pi^*)$	ϵ_1	$\log \epsilon_1$	$\lambda_2(n \rightarrow \pi^*)$	$\log \epsilon_2$	Solvent
(38)	238	7900	3.90	sh 290 ?	≈ 1.5	n-hexane
(39)	239.5	6400	3.81	sh 290	≈ 2.2	cyclohexane
(40)	235	7500	3.88	sh 290	≈ 2.7	n-hexane
(17), R=(CH ₃) ₃ C ^[19a, 122]	228	10600	4.02	sh 310-320	≈ 2.8	n-heptane
(17), R=(CH ₃) ₂ CH ^[18d]	227.5	5000	3.70			"
(17), R=CH ₃ ^[19a, 114]	225-6	10300	4.01	sh 295-310	≈ 2.9	"

[120] M. van Meerssche, University of Louvain.

[121] W.D. Wilk, A.L. Allred, B.A. Koven and J.A. Marshall, J. Chem. Soc.(London) B 1969, 565.

[122] This work.

[123] E.A.V. Ebsworth and S.G. Frankiss, J. Chem. Soc.(London), 1963, 661.

From table 4 and fig. 18 it is seen that nitroacetylenes absorb at wavelengths 10 nm longer than the corresponding nitroolefins. The extinction coefficients are slightly lower. These are common features of acetylenic systems when compared with their ethylenic analogues^[124]. Along with the main absorption, due to a $\pi \rightarrow \pi^*$ transition of the $-C \equiv C-NO_2$ system (K-band), shoulders at 290 nm are found. These may be attributed to the known weak $n \rightarrow \pi^*$ transition of the nitro group (R-band)^[114, 124].

IR spectra of the nitroacetylenes (38)-(40) are significant and simple. The triple bond, nitro group and other absorption bands are listed below.

Table 5. Characteristic IR Absorptions of Nitroacetylenes
(38)-(40)

Vibration		(38)	(39)	(40)
C $\equiv$ C stretching	strong	2235	2245	2260
	weak	2270	sh 2210	2200
NO ₂ stretching	asym.	1515	1510	1515
	sym.	1350	1345	1358
900-700 cm ⁻¹				835
region, all		844	878	826
medium intensity		737	780	770
		730	730	730

^[124] R.M. Silverstein and G.C. Bassler, "Spectrometric Identification of Organic Compounds", 2nd ed., J. Wiley & Sons, Inc., New-York-London-Sydney, 1968, p. 148 ff.

In table 6 the $C\equiv C$ absorptions of some tert-butylacetylenes with substituents X out of the first and higher periods are shown. Theoretically it seemed not possible to predict position and intensity of the triple bond vibrations in nitroacetylenes when these were still unknown^[10].

Table 6. Infrared Triple Bond Absorptions of tert-Butylacetylenes t-Bu-C $\equiv$ C-X.

X	C $\equiv$ C Absorption		Reference
H	2105 w		[125] and this work
CONH ₂	2245 m	2220 m	this work
COOEt	sh 2260 m	2230 ms	"
CN	2325 w	2270 vs	"
N(CH ₃) ₂	sh 2260 m	2230 s	"
N(C ₆ H ₅)CH ₃	2280 w	2245 s	"
NO ₂	2270 w	2235 vs	"
Cl	2243 w	2170 wm	[126]
Br	2216 vw		"
I	2191 vw		"

[125] N. Sheppard and D.M. Simpson, Quart. Reviews 6, 1 (1952).

[126] a) loc. cit.[42], p. 78.

b) S.Y. Delavarenne, H.G. Viehe and J.R. Senders, unpublished results.

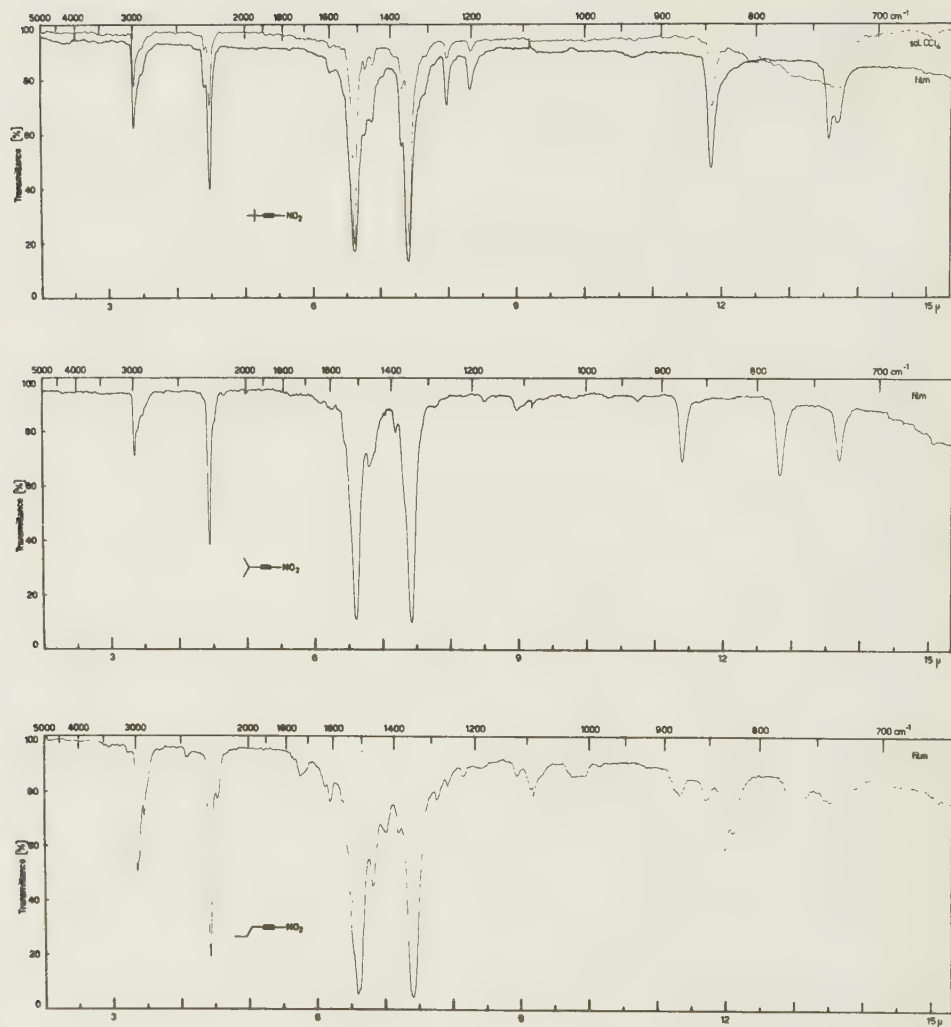


Fig. 19. IR spectra of *tert*-butylnitroacetylene (38), isopropylnitroacetylene (39) and n-propylnitroacetylene (40).

From table 6 it can be seen that first row elements give rise to medium-strong split absorptions. The weaker bands or shoulders appear at higher wave numbers. Inversely polarized systems like ynamines and nitroacetylenes absorb at nearly the same position and both these absorptions are very intense. If one compares the intensities of the C-H stretching vibrations of the tert-butyl groups in the $3000\text{-}2800\text{ cm}^{-1}$ region with those of the acetylenic bands, the nitroacetylenic absorption of the triple bond may be seen to be the most intense followed by that of the cyano derivative. However, when the tert-butyl central carbon is replaced by a second period element as silicon, represented by trimethylsilylnitroacetylene, the $\text{C}\equiv\text{C}$ absorption becomes quite weak and appears at lower wave numbers (2165 cm^{-1})^[127].

The split $\text{C}\equiv\text{C}$ absorption is characteristic for disubstituted acetylenes, its origin is still subject to discussion^[116, 124, 125]. In the nitroacetylene series (38)-(40) an inversion of the weaker band is observed: in (38) it appears at higher wave numbers than the main band ($2270\text{ vs. }2235\text{ cm}^{-1}$), in (39) and (40) at lower wave numbers (see table 5 and fig. 19).

The nitro group absorption modes for saturated, olefinic and aromatic nitro compounds have been summarized in the fundamental paper of J.F. Brown, Jr.^[115a] Aliphatic nitro compounds exhibit a symmetric NO_2 stretching mode of only medium intensity. They therefore can be easily distinguished from unsaturated nitro compounds where this absorption equals approximately the intensity of the

^[127] R. Verbruggen, Mémoire de Licence, Univ. Louvain 1970.

asymmetric vibration. The latter is usually found to be very strong. In the nitroacetylenes (38)-(40) the symmetric NO_2 stretching mode appears slightly stronger than the asymmetric one at $1510\text{-}1515\text{ cm}^{-1}$. Both conjugation and electronegativity of the adjacent carbon atom seem to lower the frequency of ν_{as} as seen in table 7 ; ν_{sym} here rests essentially unchanged.

Table 7. NO_2 IR Stretching Modes (cm^{-1}) in Hydrocarbon Derivatives.

Compound (R=tert-butyl)	ν_{as}	ν_{sym}	Ref.
$\text{C}_2\text{H}_5\text{-NO}_2$	1557 vs	1368 m	[115]
trans-R-CH=CH- NO_2	1530 vs	1357 vs	[19a], this work
R-C $\equiv$ C- NO_2	1515 vs	1350 vs	this work
$\text{C}_6\text{H}_5\text{NO}_2$	1530 vs	1353 vs	[115], [124]

There has been some controversy what concerns the position of further C- NO_2 vibrations in the $1000\text{-}700\text{ cm}^{-1}$ region, cp. lit. [42, 115, 116, 124]. From the nitroacetylene series (38)-(40) in this region only the 730 cm^{-1} band is constant in all three compounds, thus it may tentatively be assigned to the C-N stretching mode (cp. table 5, and fig. 19).

IV. Reactions of Nitroacetylenes.

1. General.

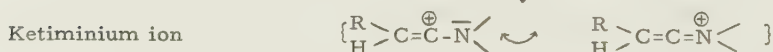
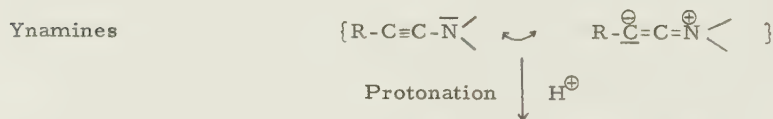
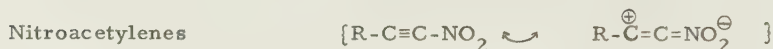
Tert-butylnitroacetylene (38) is the most stable nitroacetylene prepared in the course of this work. Therefore (38) was chosen as a model compound to study the reactions of this new class of compounds. Although the tert-butyl group protects unstable systems rather efficiently, this bulky substituent is known to decrease the reactivity of neighbouring functional groups. This is the case especially in reactions that are very sensitive to steric effects like the Diels-Alder addition. In spite of this, the reactions described in this chapter and carried out mostly with (38), all proceed without catalysts at temperatures between -30 and 20°. Thus the enhanced reactivity of the electrophile triple bond, compared with other hetero-substituted acetylenes^[8b] or with their ethylenic analogs, nitroolefins^[19, 20, 128], is clearly demonstrated. The corresponding adducts are mostly formed quantitatively. In practice the yields are determined by the volatility of the products or by their readiness to crystallize. Tert-butyl compounds sometimes are difficult to crystallize because of their enhanced solubility even in hydrocarbon solvents.

Apart from the reduction of the nitroacetylenic system by catalytic hydrogenation or hydrides two reaction types may be distinguished in which the nitro group a) remains intact, or b) is transformed. Reactions of type b have been found to proceed with ynamines^[6] and with hydrazines^[129].

^[128] A. V. Topchiev, "Nitration of Hydrocarbons and Other Organic Compounds", Pergamon Press, London-New York-Paris-Los Angeles, 1959.

^[129] V. Jäger and H. G. Viehe, unpublished results 1969.

The directiochemistry^[8a] of nitroacetylene reactions is determined by the electrophile β -carbon. This comes out very plain from the charge-separating mesomeric form. From ynamines it is known that the polar ketiminium structure is of predominant importance for the direction of added molecules^[8]. Consequently, protons are added directiospecifically in the β -position. The resulting ketiminium ion in fact is the common intermediate when protic molecules HZ are added^[8]:



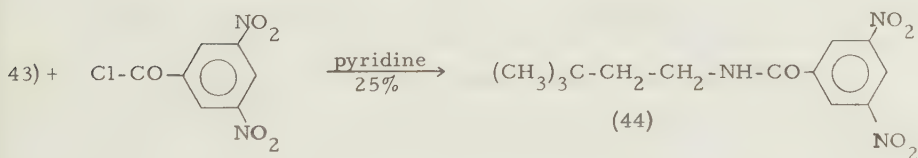
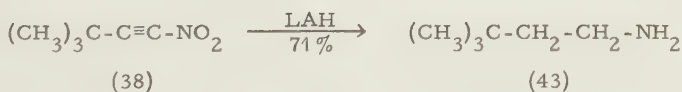
The reactions of nitroacetylenes sometimes were very exothermal, for example with nitrogen bases. Therefore all reactions described were carried out in dilute solutions, dry ether being preferred. However, as already stated in B-III/1, reactions with tert-butylnitroacetylene at higher temperatures are also possible without substantial decomposition of the nitroacetylene^[119].

[130] The principle of "Directiospecificity" and "Directioselectivity" in addition, elimination and substitution reactions of multiple bonds has been pointed out by H. G. Viehe, *Angew. Chem.* 79, 744 (1967); *ibid. internat. Edit.* 6, 767 (1967). Instead of "Directio" the term "Regio" has been used by A. Hassner in describing these phenomena [131].

[131] A. Hassner, *J. org. Chem.* 33, 2684 (1968).

2. Chemical evidence of the tert-butyl nitroacetylene structure as shown by lithium aluminum hydride reduction^[1].

After the synthesis of the first nitroacetylene (38) chemical support of its structure had to be found. The catalytic hydrogenation with platinum oxide gave a mixture of the expected saturated amine (43) and, according to NMR spectra, a "dimeric" species, N-3, 3-dimethyl-1-amino-2-butyl-N-3, 3-dimethyl-1-butylamine^[117]. The reaction with excess LAH in ether smoothly afforded the amine (43) which has previously been reported in the literature^[132]. (43) was identified by its spectral data, its boiling point was in accordance with^[132]. As the primary amine (43) was rather volatile and absorbed readily CO₂, no fitting elemental analysis could be obtained. Therefore (43) was further characterized by acylation with 3, 5-dinitrobenzoyl chloride :



The structure of (44) was established by analysis and spectra. The NMR spectrum in D₆-DMSO showed multiplets for the aliphatic protons at 1.2-1.7 and 3.2-3.6 ppm (-CH₂-N<), the amide hydrogen appeared at δ = 1.0 ppm and was exchanged on addition of trifluoroacetic acid.

^[132] A. P. Howe and H. B. Hass, Ind. Engng. Chem. 38, 252 (1946).

Thus the t-Bu-C-C-N unit is proven confirming finally the nitroacetylene structure of (38). Similar results were obtained, when the piperidine and cyclopentadiene adducts, resp., were reduced and benzoylated (part B-IV/6 and B-IV/10, resp.).

3. Addition of bromine to tert-butyl nitroacetylene.

The reaction of bromine with the nitroacetylene (38) in chloroform was slightly exothermal : on adding both solutions the mixture warmed up to about 40°. The corresponding 1,2-dibromo-1-nitroethylene (37) was isolated in almost quantitative yield :



Only one isomer is found according to the NMR spectrum of (37) ; in CCl_4 there is one peak from the tert-butyl protons which appears quite downfield at 1.50 ppm (cp. B-III/2). The geometrical relationship in (37) can not be clarified from its UV and IR spectra, fig. 12, 14, p. 69 and 70), as already discussed in B-I/4. Moreover, no conclusion can be made from the literature as the stereochemistry of halogen additions to electrophilic olefins has not yet been investigated in detail.

The addition of bromine to all but the most deactivated olefins and acetylenes is considered to be an electrophilic addition^[73]. Direct evidence has been provided for the existence of bridged bromonium cations from olefin substrates by NMR studies^[133]. The second

[133] G. A. Olah and J. M. Bollinger, J. Amer. Chem. Soc. 89, 4744 (1967) ; *ibid.* 90, 947 (1968).

bromine then adds in a trans manner. However, both electron-donor and acceptor substituents in tolane have been reported to accelerate bromine addition^[134a]. The conclusion that the primary step in these non-catalysed reactions is the addition of a nucleophile, was generalized recently^[134b]. In the case of nitroolefins and nitroacetylenes the matter is further complicated because acid catalysis^[135] by traces of HBr or HCl (from chloroform) cannot be excluded. The bromine attack then represents a nucleophilic addition, the result being a 1.4 addition to the conjugated system. The lack of experimental facts does not permit to predict the stereochemical consequences of both catalysed and uncatalysed bromine additions to multiple bond systems.

Polyhalonitroolefins are barely known in the literature^[61b]. The synthesis of trichloronitroethylene from dichloroacetylene and nitril chloride has been published, but no spectral data were given^[95b]. Apparently 1,2-dibromo-1-nitroethylenes have not been prepared up to date.

4. Addition of water and alcohols to tert-butylnitroacetylene.

a) Addition of water.

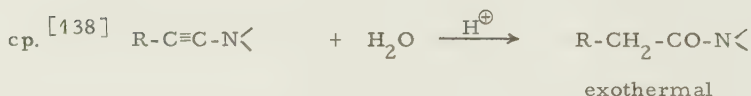
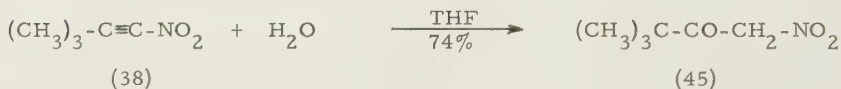
The lower members of the nitroolefin series are polymerized already by water^[21, 22]. When conditions are chosen, under which polymerization

^[134] a) H. Sinn, Angew. Chem. 69, 754 (1957).

b) H. Sinn, S. Hopperdietzel, and P. Sauermann, Mh. Chem. 96, 1036 (1965).

^[135] loc. cit. ^[15a], p. 622 ff.

is avoided, water adds to the double bond and further cleavage to the carbonyl compound and nitroalkane occurs. This reaction is reversible under basic conditions representing aldol and retro-aldol type reactions^[64,136]. The intermediate nitroalcohol has been isolated under acidic conditions, that is for example treating nitroethylene with cold dilute sulfuric acid^[137]. The nitroacetylene (38) underwent hydration of the triple bond much easier without any polymerization. A solution of (38) in tetrahydrofuran with some water had reacted completely within 24 hours at room temperature, yielding 3,3-dimethyl-1-nitro-2-butanone (45) :



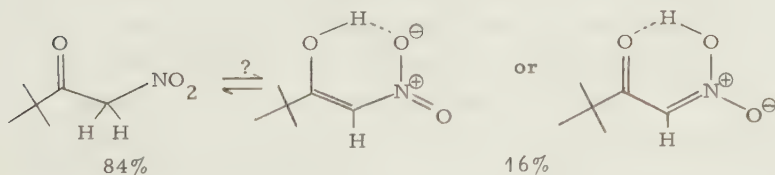
[136] L. Haitinger, Liebigs Ann. Chem. 193, 374 (1878).

[137] H. Wieland and E. Sakellarios, Ber. dtsh. chem. Ges. 52, 898 (1919).

[138] a) V. Wolf and F. Kowitz, Liebigs Ann. Chem. 638, 33 (1960).
 b) R. Buijle and H. G. Viehe, Angew. Chem. 76, 572 (1964);
 ibid. internat. Edit. 3, 582 (1964).

Thus the inversely polarized acetylenes as ynamines and nitro-acetylenes add water^[8a, 138] (and other nucleophiles, see following paragraphs) with comparable ease. The directiochemistry, of course, is inverse. The resulting α -nitro ketone (45) did not form hydrazone derivatives under conditions reported for α -nitro ketones with less bulky substituents^[139]. This may be due to sterical hindrance by the tert-butyl group.

Another phenomenon may also be attributed to the influence of the tert-butyl group. In a recent study about the structure of α -nitro ketones, it was found by NMR spectroscopy that only the cyclic derivatives isomerize partially to the enolic forms, acyclic analogs existing completely in the non-conjugated nitro ketone form^[140]. Similar results have been concluded from IR and UV spectroscopic investigations of ω -nitroacetophenone at different pH values^[141]. The NMR spectrum of (40) in CCl_4 , however, reveals two tert-butyl groups at 1.22 and 1.24 ppm, ratio 16:84. Downfield singulets at 6.75 (olefinic proton, cp. p.) and 5.38 ppm in 8:92 ratio are seen. The value of 5.38 ppm for the aliphatic protons agrees well with that of 5.28 found for 1-nitro-2-pentanone^[140]. Our findings are explained by the presence of a tautomeric nitro-enol form :



[139] C. Hurd and M. E. Nilson, J. Org. Chem. 20, 927 (1955).

[140] T. Simmons, R. F. Love, and K. L. Kreuz, *ibid.* 31, 2400 (1966).

[141] S. Deswarte, Bull. Soc. chim. France 1969, 534.

Similar peaks are observed in DMF at room temperature, the olefinic proton appears at 8.0 and the aliphatic at 6.07 ppm, but the 8.0 ppm peak has been too small for exact integration. Cooling this solution down to -35° shifts the down-field peaks to 8.16 and 6.38 ppm, resp., the tautomer ratio is $\approx 16:84$ as above in CCl_4 at room temperature.

The low tendency of α -nitro ketones to enolize has been interpreted in terms of the known weak hydrogen bonding ability of aliphatic nitro compounds^[140]. To account for this, Schleyer has pointed out that the nitro group is an electron-demanding rather than an electron-rich function^[142], in contrary to the oxygen atom in carbonyl derivatives for example. In our case, the normally stable trans nitro ketone structure^[140] has enhanced ground-state energy because of the interaction with the tert-butyl group. The energy difference between the tautomers decreases and thus appreciable amounts of an enolic isomer exist in the equilibrium.

The UV spectra of (45), see fig. 22, can be rationalized likewise. In n-hexane a maximum at 298 nm is observed with an extinction coefficient of 2900, which is unusually high for keto or nitro groups^[124]. In methanol this band is shifted to 325 nm, ϵ decreases to 670. It can be assumed that in the non-polar solvent n-hexane some enolic tautomer is present, as this absorption is comparable to that of enolized β -diketones^[124]. Methanol favours intermolecular hydrogen bonds. Thus less enol form is present. The 325 nm absorption band of low

[142] W. F. Baitinger, P. von R. Schleyer, T. S. S. R. Murty, and L. Robinson, *Tetrahedron* 20, 1635 (1964).

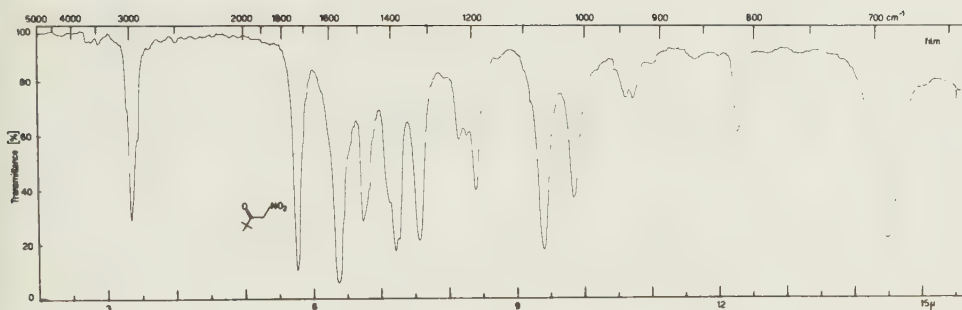


Fig. 20. IR spectrum of 3,3-dimethyl-1-nitro-2-butanone (45)

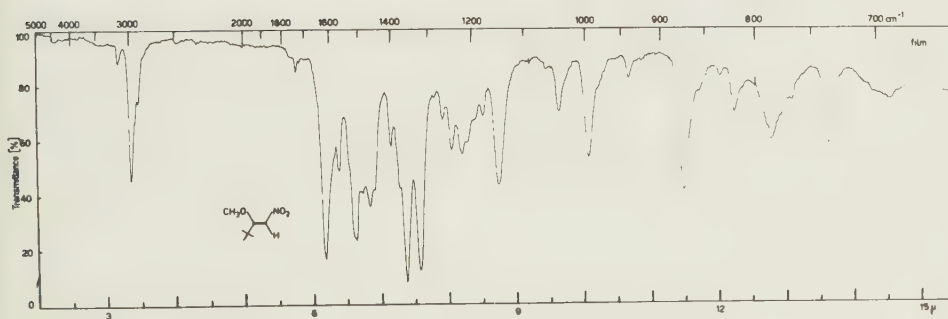


Fig. 21. IR spectrum of cis-3,3-dimethyl-2-methoxy-1-nitro-1-butene (46a)

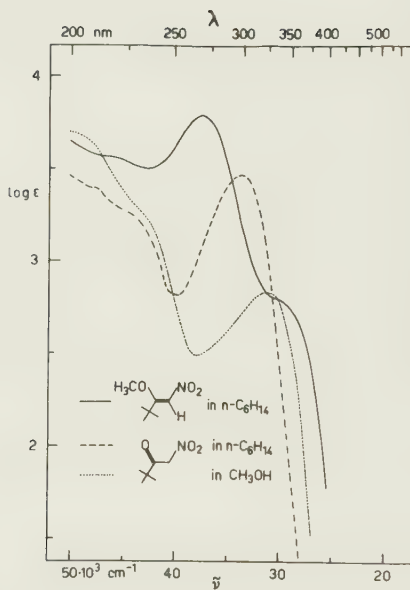


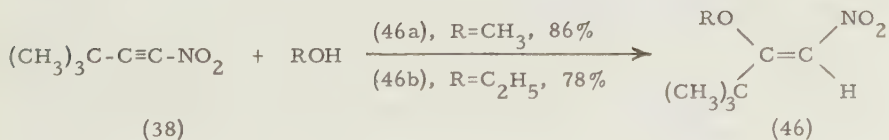
Fig. 22. UV spectra of (45) and (46a).

intensity may be explained by a small amount of enol present. Likewise it may be interpreted as arising from isolated carbonyl and/or nitro groups^[124]. Similar results have been obtained by Deswarte, when he checked the solvent dependence of the UV spectrum of ω -nitroacetophenone. The 330 nm band ($\epsilon = 7000$) of an n-hexane solution was shifted to 345 nm in chloroform, the ϵ value decreased to 3000^[141].

The characteristic frequencies and intensities of carbonyl and nitro groups in the IR spectrum of (45), fig. 20, correspond to the values given for ω -nitroacetophenone^[141]. No enolic OH stretching vibration can be found when the spectrum of (45) is taken as a film of the pure liquid.

b) Addition of alcohols.

Whereas base catalysis has been applied to add alcohols to the nitroolefinic double bond^[19a, 21], with (38) in spite of its unfavourable tert-butyl group smooth additions were observed to proceed without catalyst. Apparently the alcohol oxygen is sufficiently nucleophile to attack the highly electrophile triple bond of the nitroacetylene. Solutions of (38) in methanol or ethanol had completely converted to the corresponding nitrovinyl ethers within 24 hours.



On distillation minor amounts of geometric isomers were formed, the main isomer was still present in about 95%.

The stereochemistry of alcohol additions to conjugated triple bonds cannot be predicted^[143]. Base-catalysed addition to acetylene dicarboxylate gave the trans adduct. From the uncatalysed addition, however, proceeding at 180-200° (!), mainly maleates were isolated^[143]. Similarly, dicyanoacetylene has been reported to add alcohols at room temperature giving rise primarily (80:20) to cis addition^[144]. As discussed below, the adducts obtained from nitroacetylene (38) derive from trans addition.

The UV spectrum of (46)^a, fig. 22, exhibits no evidence for cis-tert-butyl and nitro groups (cp. B-I/4). Compared with nitroolefins and 2-X-nitroolefins the maxima of (46a) show a moderate bathochromic shift as to be expected from electron donor substituents (see table 8).

Table 8. UV absorptions of 2-X-1-nitroolefins $(\text{CH}_3)_3\text{C}-\text{CX}=\text{CHNO}_2$ (X and NO_2 cis).

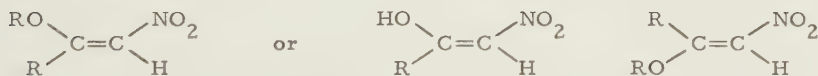
Compound, X	$\lambda_1(\log \epsilon_1)$	$\lambda_2(\log \epsilon_2)$	$\lambda_3(\log \epsilon_3)$	solvent
(17d), H	228 (4.02)		sh 310-320 (2.8)	n-heptane
(35b), Cl		246 (3.80)	sh 300 (2.4)	n-hexane
(26b), I	208 (3.8)	279 (3.46)		"
(46a), OCH_3	sh 220 (3.55)	268 (3.69)	sh 335 (2.8)	"
(46b), OC_2H_5	sh 220 (3.67)	267.5 (3.88)	sh 335 (2.9)	"
(47), $\text{N}(\text{CH}_2)_5$	228.5 (3.92)	366 (3.78)		"

[143] E. Winterfeld in loc. cit. [8b], Chapter 4 (Ionic Additions to Acetylenes).

[144] E. Winterfeld, W. Krohn, and H. Preuss, Chem. Ber. 99, 2572 (1966).

From the very similar IR spectra of (46a) and (46b) the marked intensity of the C=C stretching absorption ($1615\text{-}1618\text{ cm}^{-1}$) may be taken as a proof for unhindered conjugation (the spectra of (46a) are given in fig. 21, 22). This is possible only in the cis derivatives. The slightly less intense band at 1505 and the strongest absorptions in the IR spectrum at 1356 and 1320 cm^{-1} probably are due to asymmetric and symmetric NO_2 and the C-O valence vibration of the vinyl ether unit. The weak absorptions at 1740 cm^{-1} are due to the nitro ketone (45) which is easily formed by hydrolysis of the nitro vinyl ethers (46).

It is not possible to assign geometrical structures to (46) from the NMR spectra. The peaks of the other, minor isomers (present in a few percent) appear only ≈ 0.03 ppm at higher field. Therefore, the method to estimate chemical shifts by addition of increments^[77, 78] fails here (cp. A-II/2) :



calculated :	5.82 ^[145]	5.90 ppm
observed : (46a)	6.6	(45) 6.75
	(46b) 6.55	

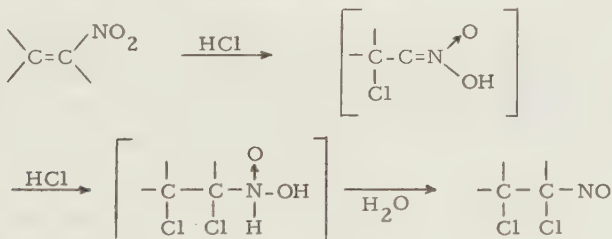
Considerable deviations between calculated and found values in other cases have been explained in terms of incomplete conjugation^[77, 78], but here this interpretation seems doubtful as the olefinic proton of the certainly strain-free (45) appears in the same region.

^[145] OH increments are not known, they should be similar to those of alkoxyl groups. Theoretically, the β -trans proton should appear at lower field in (45) compared with (46) as observed here.

Nitrovinyl ethers seem to be unknown in the literature. Those prepared here are slightly yellow, stable liquids ; the strong lachrymatory odour of nitroolefins or halo-nitroolefins is no longer present. The above nitrovinyl ethers pass undecomposed in GLC analysis. Acid or base-catalysed hydrolysis proceeds readily, as seen for example on recording their infra-red spectra.

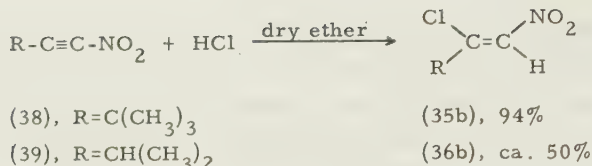
5. Addition of hydrogen chloride to nitroacetylenes.

The reaction of nitroolefins with anhydrous hydrogen chloride in ether has been reported to consist of a rather complicated reaction sequence^[21]. From nitroolefins containing no α -hydrogen atom, the final products have been identified as 1,2-dichloro-1-nitrosoalkanes^[146]. The reactions did not proceed quantitatively. After 20 hours at room temperature starting products were still present. The first step of these reactions has been shown to be 1,4-addition of HCl to form a nitronic acid. Addition of a second mole of HCl and loss of water produced the nitroso compound^[146] :



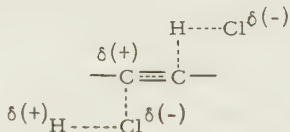
Nitroacetylenes behave differently. Excess HCl under similar conditions added smoothly to the triple bond. The addition products, 2-chloro-1-nitroolefins, were formed quantitatively. This was proven when immediately after mixing ethereal solutions of (38) and hydrogen chloride the infrared spectrum of the mixture was recorded. The triple bond absorption had disappeared. Only the addition product (besides excess HCl) was present. This was found later when an IR spectrum of the isolated product was compared with that of the above mixture.

^[146] R. L. Heath and J. D. Rose, J. Chem. Soc. 1947, 1485.



According to the NMR spectra and GLC analyses these additions proceed in a stereospecific manner. The cis isomers (35b) and (36b) are formed by trans addition exclusively. Spectra and configurational assignment of (35b) and (36b) have already been discussed in part B-I/4.

In principle 1,4 addition of HCl to nitroacetylenes should lead to subsequent reactions similar to that of nitroolefins. However, none of these are found to take place. The nitro group remains unchanged. It is probable that in the case of nitroolefins a different mechanism is involved. Trans addition of hydrogen chloride to triple bonds usually is regarded as a consequence of an $Ad_E3^{[*]}$ mechanism. One of the possible transition states may be represented as follows [73].



[*] Addition, electrophile, 3rd order kinetics

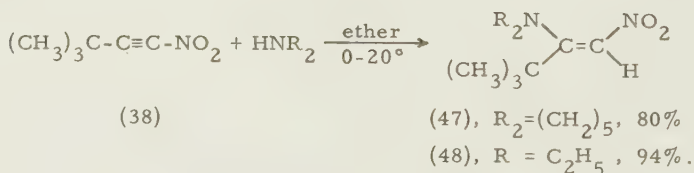
Rate studies should allow to distinguish between the above mechanisms or a more probable possibility, initiation by a nucleophilic attack^[73, 143]. The latter process has been proven to be the first step, when hydrogen halides are added to activated acetylenes such as acetylene dicarboxylates^[143, 147]. The addition is completed by rapid protonation. As nitroacetylenes should be even more electrophile systems, it seems reasonable to assume that HCl additions here take a similar course.

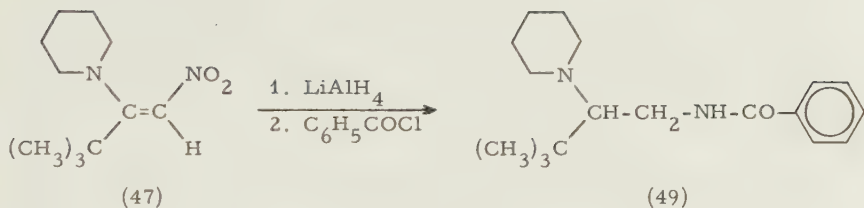
-
- [147] a) G.F. Dvorko, Dopovidi Akad. Nauk Ukr. R.S.R. 1959, 498; C.A. 54, 2162c (1960).
b) Part 14 of the series "Theorie of Nucleophilic Additions", G.F. Dvorko and D.F. Mironova, Ukr. Khim. Zh. 31, 195 (1965); C.A. 63, 2865g (1965); and preceding papers.

6. Nitroenamines from the reaction of tert-butyl nitroacetylene with primary and secondary amines.

In a thorough investigation Heath and Rose have shown that the addition of ammonia, primary and secondary amines to nitroolefins in general proceeds easily^[22a]. From the highly reactive nitroethylene with aromatic amines addition has been stated. More basic aliphatic amines, however, gave rise to extended polymerization^[22b].

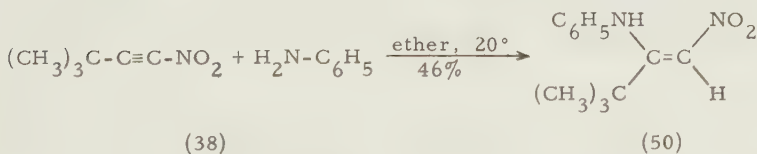
Similarly, aliphatic amines such as piperidine led to decomposition of tert-butyl nitroacetylene (38), when both were undiluted. However, this was a very exothermal reaction even with milligram quantities, the mixture sometimes bursting into flames (see "Properties", B-III/1). When the reaction was run in ether at 0° and the ethereal solution of (38) dropped slowly to the amine solution, no decomposition occurred. The corresponding nitroenamine (47) crystallized on evaporation of the solvent. Inverse addition gave an oil that contained a few percent of another unidentified product along with approximately 95% of (47). This was seen from the NMR spectrum of the crude product. Diethylamine likewise yielded a single isomer (48).





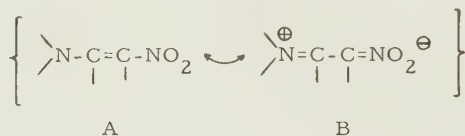
The expected direction of amine addition to yield (47) – at the same time another chemical evidence for the structure of (38) – was proven by LAH reduction and subsequent benzylation. Analytical and spectral data of (49) were in accord with the given structure.

From the reaction of (38) with a primary aliphatic amine – aniline –, only 46% of a crystalline adduct could be isolated, though the reaction was shown by IR spectroscopy to be complete. This may have been due in part to the presence of the tautomeric more soluble imine form.



Nitroenamines are a very recent class of compounds^[148]. The different routes for their preparation have been surveyed by Freeman and Emmons in 1956^[149]. A generally applicable method for the synthesis of 2-substituted 2-nitroenamines has been developed by Meerwein and coworkers^[150].

Nitroenamines represent well-stabilized push-pull systems that are best described by two canonical structures:



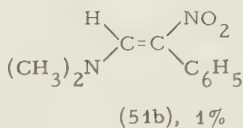
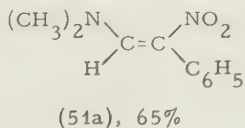
The amino group is a strong electron-donor as well as the nitro group is a powerful electron-acceptor. The mesomeric form B therefore contributes to the resonance hybrid an important share. This is perceived from their physical properties as high melting points, slight solubility in non-polar solvents, colour and spectral data, which are discussed below. In contrast to the amine adducts of nitroolefins^[21, 22], nitroenamines form stable yellow-orange or orange-red crystals.

[148] C.D. Hurd and L.T. Sherwood, J. Org. Chem. 13, 471 (1948).

[149] J.P. Freeman and W.D. Emmons, J. Amer. Chem. Soc. 78, 3405 (1956).

[150] H. Meerwein, W. Florian, N. Schön and G. Stopp, Liebigs Ann. Chem. 641, 1 (1961).

The structure of nitroenamines, especially of those derived from primary amines, has been subject to several UV and IR spectroscopic investigations. Unfortunately, up to date NMR spectra of unsubstituted nitroenamines have not yet been published in order to confirm previous structure assignments. Freeman and Emmons prepared secondary and tertiary nitroenamines by several methods. The UV spectra of all the compounds examined were of the same general shape^[149]. Two principal absorption bands at ≈ 235 (nitroolefin portion) and at 355-390 nm (from the mesomeric form B) have been recorded. Thus it has been shown that compounds such as (50) with an NH group exist in the enamine rather than in the imine form^[149]. Furthermore, from UV and IR spectra it has been proven that secondary nitroenamines such as (50) form chelates. This is only possible with cis amino and nitro groups. From the similarity of the spectra it has been concluded that all the compounds prepared thus far have the cis configuration. Similar results were reported later^[151, 152]. Recently from the preparation of the yellow 1-nitro-2-dimethylamino-1-phenylethylene (51a) a second, red isomer (51b) has been isolated. From the UV spectral data (see table 9) the latter was assigned to the trans structure^[153].



[151] R.D. Campbell and F.J. Schultz, J. Org. Chem. 25, 1877 (1960).

[152] F.W. Lichtenthaler and N. Majer, Tetrahedron Letters 1969, 411.

[153] T. Severin and H.J. Böhme, Chem. Ber. 101, 2925 (1968).

The UV spectra of the nitroenamines (47), (48) and (50) of the present work fit closely to those reported^[149, 151]. They all belong to the cis series. This may also be concluded as the characteristic features of cis tert-butyl and nitro group are not found in these UV spectra. Because of the important steric t-butyl - NO₂ interaction the isolated derivatives should also be the thermodynamically favoured isomers. The UV data of some nitroenamines are listed in table 9 (cp. also UV spectra of (CH₃)₃C-CX=CHNO₂ derivatives, table 8, p.102). The UV spectra of (47) and (50) are seen in figs. 23 and 24. The UV absorptions of (50) depend strongly on the pH of the solution, as represented in fig. 24. Hydrogen chloride or alkali both affect the chromophoric system, but here irreversible chemical reactions may be involved.

Table 9. UV Absorptions of Nitroenamines.

Compound	Solvent	λ_1 (log ϵ_1)	λ_2 (log ϵ_2)	References
R-CH=CH-NO ₂		225-230 (3.8-4.0)		[19, 79, 114]
R-CH=CH-NR ₂		225-230 (3.7-3.9)		[154]
(47)	n-hexane	228.5 (3.92)	366 (3.78)	this work
(48)	CH ₃ OH	227 (3.91)	385 (4.15)	"
(50)	CHCl ₃	236 (3.86)	358 (4.29)	"
	CH ₃ OH	240 (3.93)	358 (4.03)	"
(51a)	"		370 (4.25)	[153]
(51b)	"		498 (3.73)	"

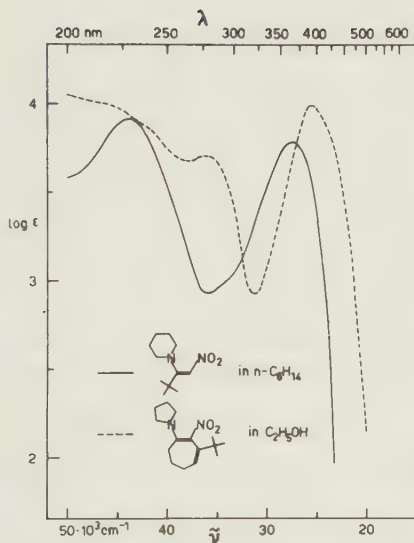


Fig. 23. UV Spectra of the Nitro-enamine (47) and the Nitrodienamine (54)

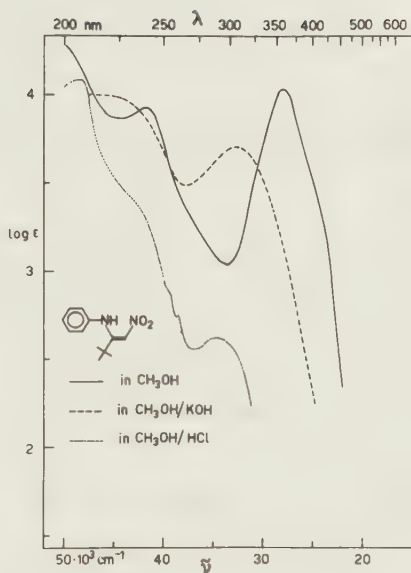


Fig. 24. UV Spectra of the Secondary Nitroenamine (50) in Acid, Neutral and Alkaline Solution.

Further, the intensity of the 358 nm absorption band in CHCl_3 solution decreases from 19000 (4.29) to 13700 (4.14) within 5 hours. This may be explained by partial isomerization to the imine tautomer (50b), which is expected to absorb at lower wave lengths.

[154] S.K. Malhotra in loc. cit.^[7], Chapter 1 (Structure and Physical Properties of Enamines).

The IR spectra of the nitroenamines prepared here do not permit a configurational assignment, see fig. 25.

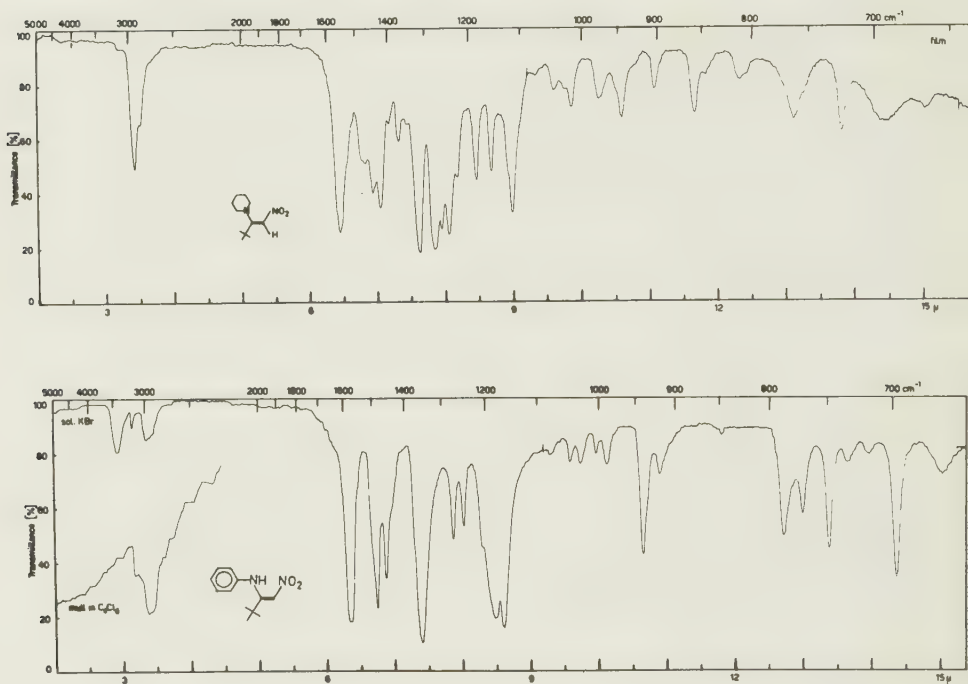


Fig. 25. IR Spectra of the Tertiary Nitroenamine (47) and the Secondary Nitroenamine (50).

Freeman and Emmons had already stated that the normal NH absorption bands were absent or displaced with strongly diminished intensity owing to hydrogen chelation^[149]. The IR spectrum of (50) in KBr or C₄Cl₆ (hexachlorobutadiene), fig. 25, corresponds with these findings. The usual stretching frequencies of the nitro group cannot be unambiguously assigned either, see fig. 25. Several strong bands in the 1600-1100 cm⁻¹ region are probably associated with the nitroenamine system. These severe changes provide further evidence that the zwitterionic structure B already contributes to a large extent to the ground state of the nitro-enamines^[149]. IR spectra of comparable systems such as enaminketones, have been reported to show similarly strong coupling and band splitting of the C=O and C=C-N< stretching vibrations^[155].

In the NMR spectra the olefinic hydrogen atoms of (47), (48), (50a) are located in the range 6.6-6.9 ppm. The values calculated by the increment method^[77-79], discussed in part A-II/2, deviate considerably from the experimental values:

	found	calc.		
		<u>cis</u>	<u>trans</u>	
(47), <u>cis</u>	6.60	5.78	5.67	$ \begin{array}{c} (\text{CH}_3)_2\text{N} \quad \text{NO}_2 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{Br} \end{array} $
(48), <u>cis</u>	6.90	"	"	
(50), <u>cis</u>	6.77	6.04	6.44	
(52), <u>cis</u> ?	8.68	7.10	8.10 ^[35]	

[155] J. Dabrowski and K. Kamińska-Trela, Spectrochim. Acta 22, 211 (1966); J. Dabrowski and U. Dabrowska, Chem. Ber. 101, 2365 (1968).

This appears to be a general feature of nitroenamines. The UV spectrum of the strain-free bromo-nitroenamine (52) exhibits a long wave length peak at 372 nm ($\log \epsilon$ 4.25)^[35]. As mentioned before, this signifies a cis arrangement of the nitroenamine unit. The above discrepancies are probably due to the ground state contribution of mesomer B in nitroenamines. The lack of NMR spectral data concerning nitroenamines does not yet allow one to account for these deviations in a satisfactory manner.

The decrease of the UV extinction of (50) in CHCl_3 solution to 72% of the original value has been rationalized by partial tautomerization. Direct evidence for this is gathered from the NMR spectrum of 50 in CDCl_3 solution. Two tautomers are present in a 2:1 ratio, the enamine form (50a) predominating. The imine form (50b) exhibits a singlet at 5.23 ppm, which is slightly downfield compared to the range of $\text{C}=\text{C}-\text{CH}_2-\text{NO}_2$ values^[79]. Likewise, an IR spectrum of (50) in CHCl_3 , compared to that taken in KBr, exhibits significant changes owing to partial isomerization. Spectroscopic investigations of similar secondary enamines conjugated with ketone, ester, nitrile^[143, 156] and phenyl groups^[157] have also established the prevalence of the enamine rather than imine-enol or imine tautomers. Even the independent isolation of a primary enamine and its tautomeric imine form has been achieved^[158].

[156] a) M.E. Kuehne in loc. cit.^[7], Chapter 8 (Enamines in Organic Synthesis);

b) N.D. Heindel and P.D. Kennewell, Chem. Comm. 1969, 757 ; and references therein.

[157] H. Ahlbrecht, J. Blecher and F. Kröhnke, Tetrahedron Letters 1969, 439, and references therein.

[158] M. Masaki, C. Shin, H. Kurita and M. Ohta, Chem. Comm. 1968, 1447.

Both exclusive cis- and trans-additions of primary and secondary amines to activated acetylenes have been reported^[143]. The stereochemistry of these additions has been shown to vary 1) with the substrates, 2) with the kinds of amines added, 3) with the solvent, and 4) with the mode of addition^[143]. As different mechanisms and often subsequent isomerizations are involved, no generalization can be made. With tert-butylnitroacetylene (38) the thermodynamically more stable isomers were always obtained. The overall process was trans addition. No deuteration experiments were performed to check the cis-trans isomerizations. Therefore it cannot be stated whether the nitroenamine stereoisomers obtained also represent the kinetic reaction products.

7. Reaction of tert-Butylnitroacetylene with Enamines.

Tert-butylnitroacetylene (38) and enamines explode into flames when the neat liquids are mixed (see also B-III/4). In dilute solution, however, the nitroacetylene (38) and enamines such as those derived from isobutyraldehyde and cyclopentanone, for example, reacted smoothly. As our intention was to establish the principles of nitroacetylene reactions, only the latter reaction was investigated in detail. When (38) was dropped to an ethereal solution of 1-pyrrolidinocyclopentene (53), an IR spectrum, recorded immediately after the addition was complete, showed that the triple bond absorption of (38) had disappeared almost completely. However, this IR spectrum differed strongly from that of the product obtained after recrystallization. This indicated the formation of a thermally unstable intermediate whose rearrangement finally led to the 1:1 adduct isolated.

[159] A.G. Cook in loc. cit.^[7], Chapter 6 (Cycloaddition Reactions of Enamines).

[160] a) J. Smuszkovicz, *Advances Org. Chem.* 4, 1 (1963) ;

b) G. Stork, A. Brizzolara, H. Landesmann, J. Smuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.* 85, 207 (1963).

[161] K.C. Brannock, A. Bell, R.D. Burpitt and C.A. Kelly, *J. Org. Chem.* 29, 801 (1964).

[162] M.E. Kuehne and L. Foley, *ibid.* 30, 4280 (1965).

[163] a) A. Risaliti and L. Merchetti, *Boll. Sci. Fac. Chim. Ind. Bologna, C. A.* 61, 10619 (1964). 22, 61 (1964) ;

b) A. Risaliti, S. Fattuta, M. Forchiassin and E. Valentin, *Tetrahedron Letters* 1966, 1821.

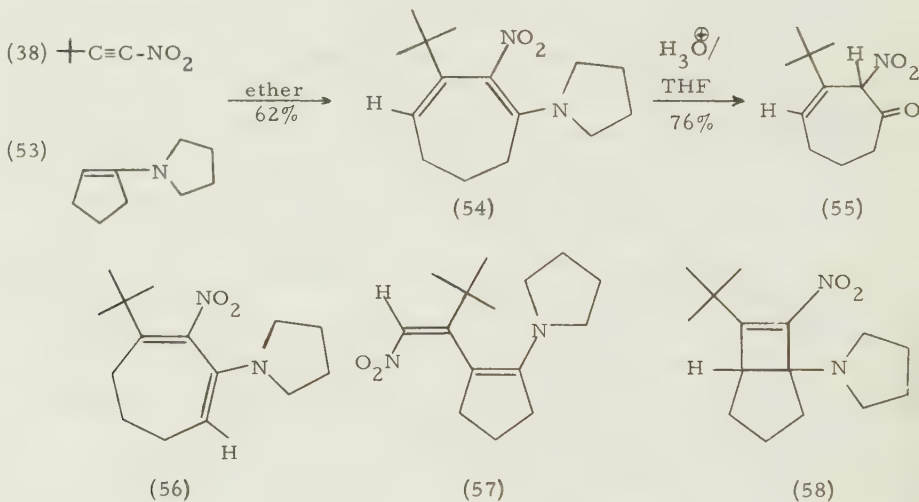
c) A. Risaliti, M. Forchiassin and E. Valentin, *Tetrahedron Letters* 1966, 6331.

Enamines are known to react with nitroolefins^[154, 156a, 159-166], other electrophilic olefins^[154, 156a, 159, 160, 167-169], and acetylenic systems^[169-173]. Similar reactions have been reported of ynamines : the formation of cyanines by "dimerization"^[8, 173-175] or their cycloadditions with electrophilic olefins^[8, 173, 176, 177]. According to the above reports four structures have to be taken into account for the 1:1 adduct from (38) and (53) :

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- [164] A. Risaliti, L. Marchetti and M. Forchiassin, *Ann. Chim. Rome* 56, 317 (1966) ; *C.A.* 65, 8901 (1966).
- [165] A. Risaliti, M. Forchiassin and E. Valentin, *Tetrahedron* 23, 1451 (1967) ; *ibid.* 24, 1889 (1968).
- [166] H. Feuer, A. Hirschfeld and E.D. Bergmann, *Tetrahedron* 24, 1187 (1968).
- [167] a) K.C. Brannock, A. Bell, R.D. Burpitt and C.A. Kelly, *J. Org. Chem.* 26, 625 (1961) ;
b) K.C. Brannock, R.D. Burpitt, V.W. Goodlett and J.G. Thweatt, *ibid.* 29, 813, 818 (1964).
- [168] A. Risaliti, E. Valentin and M. Forchiassin, *Chem. Comm.* 1969, 233.
- [169] G.A. Berchtold and G.F. Uhlig, *J. Org. Chem.* 28, 1459 (1963).
- [170] a) K.C. Brannock, R.D. Burpitt and J.G. Thweatt, *ibid.* 28, 1462 (1963) ;
b) K.C. Brannock, R.D. Burpitt, V.W. Goodlett and J.G. Thweatt, *ibid.* 28, 1464 (1963).
- [171] C.F. Huebner, L. Dorfmann, M.M. Robinson, E. Donoghue, W.G. Pierson, and P. Strachan, *ibid.* 28, 3134 (1963).
- [172] E. Yoshii and S. Kimoto, *Chem. Pharm. Bull. (Tokyo)* 17, 629 (1969).
- [173] R. Fuks and H.G. Viehe in *loc. cit.*^[8b], Chapter 8 (Cyclic Compounds from Acetylenes).

- 1) the cycloheptadiene derivative^[169-173] (54),
- 2) its tautomer^[169, 172] (56),
- 3) the Stork alkylation product^[160, 162, 163, 165b, 166, 167b, 170a] (57), and
- 4) the cyclobutene derivative^[161, 162, 167, 168, 171, 173-176].

Spectral data and chemical transformation of the 1:1 adduct into the α -nitro ketone (55) by mild hydrolysis of the enamine function established the cycloheptadiene structure (54) :



- [174] a) J. Ficini and C. Barbara, *Tetrahedron Letters* 1966, 6425 ;
- b) H.G. Viehe, R. Buijle, R. Fuks, R. Merényi and J.F.M. Oth, *Angew. Chem.* 79, 53 (1967) ; *ibid. internat. Edit.* 6, 77 (1967) ;
- c) L. Ghosez, B. Haveaux and H.G. Viehe, *Angew. Chem.* 81, 468 (1969) ; *ibid. internat. Edit.* 8, 454 (1969).
- [175] a) R. Gompper and G. Seybold, *Angew. Chem.* 80, 804 (1968) ; *ibid. internat. Edit.* 7, 824 (1968) ;
- b) M. Neuenschwander and A. Niederhauser, *Chimia* 22, 491 (1968).

The NMR spectrum of the 1:1 adduct, given in fig. 26, is only consistent with the cycloheptadiene structure (54). The olefinic proton appears at 6.04 ppm as a diffused triplet, $J \approx 6.5$ cps. The smaller coupling constants could not be determined. A J value of 6.5 cps clearly eliminates the alkylation product (57) in which the long range coupling of the olefinic proton would be less than 3 cps^[124]. In (58) there would be no vinyl absorption at all. The tautomeric cycloheptadiene (56) would be expected to have its vinyl proton located as high as 4.5-5.0 ppm^[172] due to the shielding effect of a trans amino group^[77, 78].

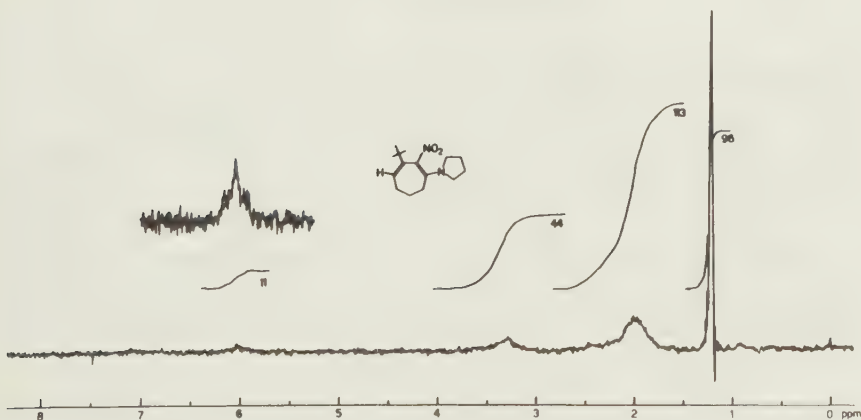


Fig. 26. NMR spectrum of 1-pyrrolidino-3-tert-butyl-2-nitro-1,3-cycloheptadiene (54).

[176] a) M.E. Kuehne and P.J. Sheeran, J. Org. Chem. 33, 4406 (1968).

b) J. Ficini and A. Krief, Tetrahedron Letters 1969, 1431.

[177] M. Franck-Neumann, Tetrahedron Letters 1966, 341.

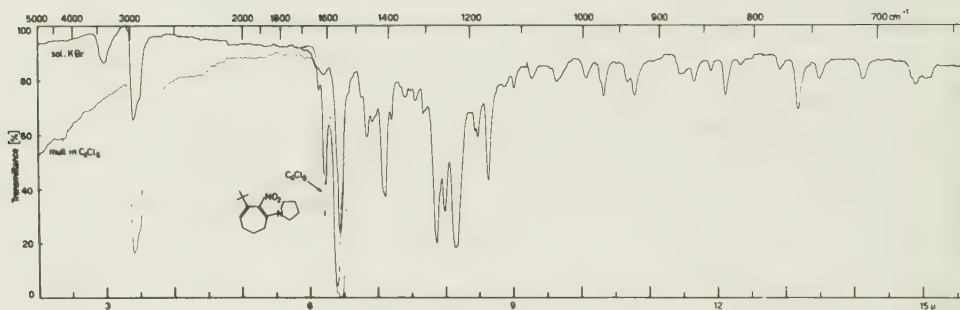


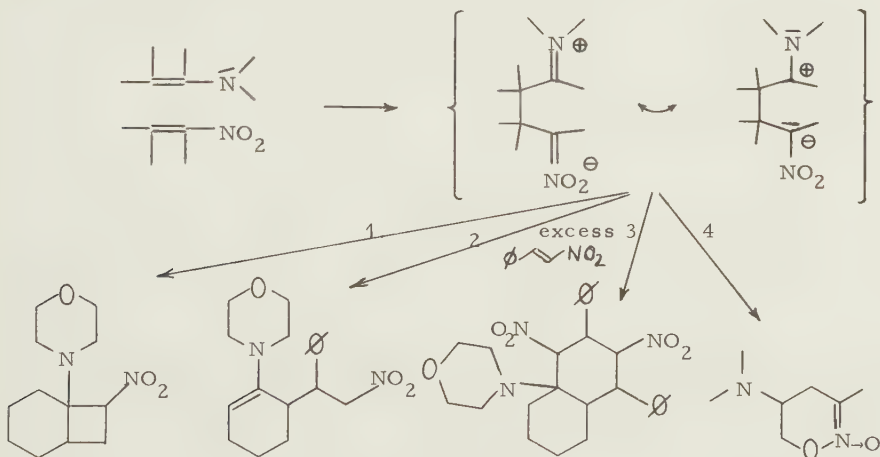
Fig. 27. IR spectrum of (54).

(54) exhibits IR absorptions similar to those of nitroenamines (cp. the IR spectrum of (54), fig. 27, with those of nitroenamines, fig. 25, p. 114). Its UV spectrum given in fig. 23, p. 113, also resembles closely those recorded for nitroenamines.

The nitro-cycloheptadienamine structure (54) is further distinguished from the alkylation product (57) by the mild acid hydrolysis of the enamine function^[151, 169-172] producing the α -nitro ketone (55). In its NMR spectrum a singlet at 5.65 ppm appears. For example, the methylene protons of α -nitro pinacolone (45) appear at 5.38 ppm, see p. 97. (55) shows strong IR absorption bands at 1720 (C=O), 1362 and 1554 (split asym. NO₂ stretching mode) and a medium 1355 cm⁻¹ band. Position and intensities of the nitro group absorptions are characteristic for a NO₂ group attached to a saturated carbon atom^[115]. No H-D exchange could be observed, when (55) was dissolved in deuterated trifluoroacetic acid. This appears reasonable,

because the intermediate nitro enol form should be unfavourably strained due to cis vicinal tert-butyl and nitro groups at sp^2 carbon atoms.

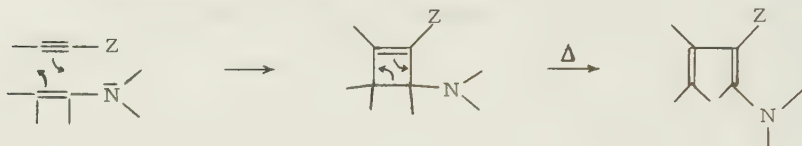
Nitroolefins and enamines may react to give four different types of products [154, 156a, 159-166]. A 1,4-dipole seems to be the common intermediate [168] (see reaction scheme). The following reactions depend on the structure of the substrates and on the polarity of the solvent.



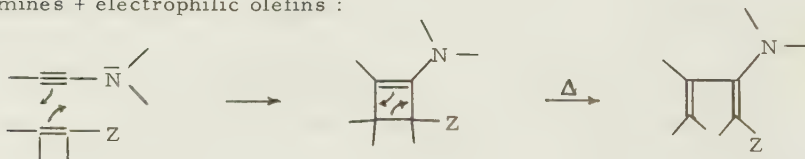
In contrast to the above two-step processes, from the reaction of enamines with acetylene dicarboxylates or propiolates the intermediate 1,4 dipoles collapse too fast to be trapped. The cyclobutene intermediates sometimes are stable enough to be isolated [167b, 169, 171], but mostly butadienes are formed by valence-bond isomerization.

Analogous reactions of ynamines are known. Ketenes^[176a], unsaturated carbonyl derivatives^[176b] and diphenylcyclopropenone^[177] give cyclo-addition or rearranged products. Similarly, the acid-catalyzed "dimerization" of ynamines yields cyclobutene cyanines^[173-175].

Enamines + electrophilic acetylenes :

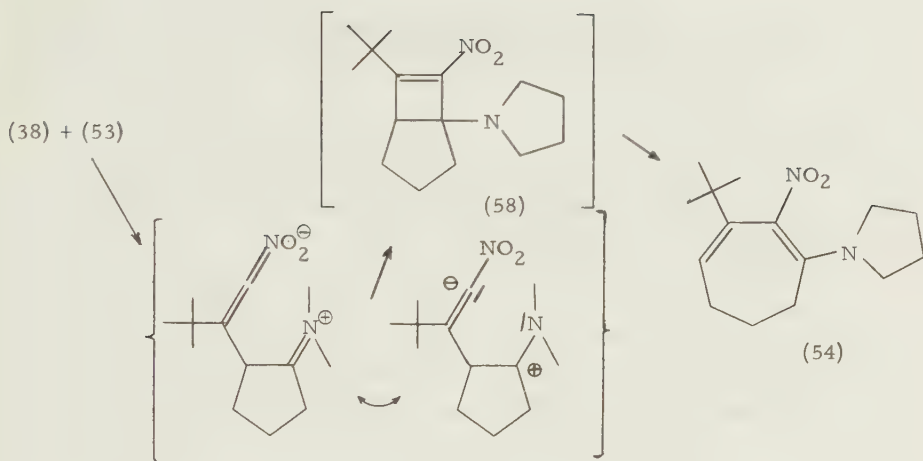


Ynamines + electrophilic olefins :



In our case, the enamine (53) and the nitroacetylene (38) already reacted at 0°. IR spectroscopic control indicated that the products first formed rearranged during its isolation. The intermediate product observed probably is the cyclobutene derivative (58). Its formation must be rationalized by a two-step process. Thermal cycloreversion of the four-membered ring^[178] (58) is facilitated because of the steric crowding of the cis tert-butyl and nitro groups.

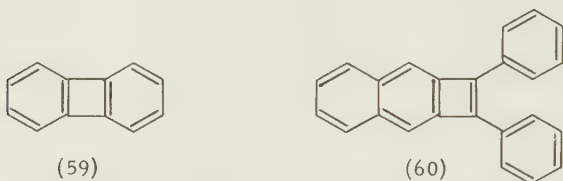
[178] R.B. Woodward and R. Hoffmann, *Angew. Chem.* 81, 797 (1969) ; *ibid. internat. Edit.* 8, 784 (1969).



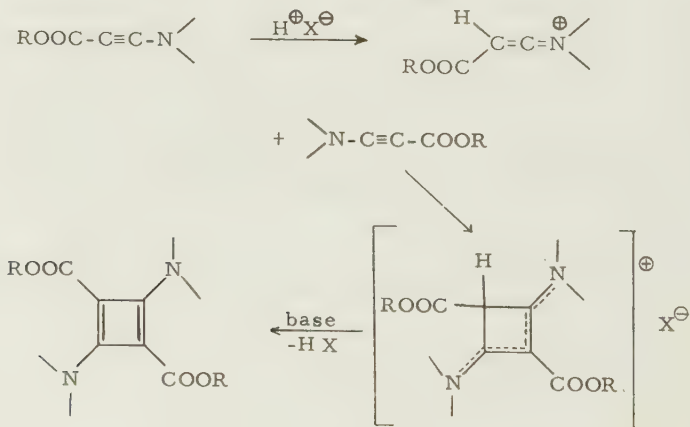
The reaction of nitroacetylenes with enamines is an example of a synthetically useful method to extend a carbon chain by a C_2 unit. Alicyclic enamines undergo a ring expansion as shown with (53). The ease of the above reaction is surprising. A similar cycloaddition of (53) with propiolates has been reported to proceed below 35° yielding the cyclobutene derivative. Heating to 90° then gave the cycloheptadiene^[167b]. Tetrolates, where the acetylenic hydrogen of propiolates is replaced by a methyl group, are much less reactive. Refluxing in toluene is necessary to start the reaction which leads to the corresponding cycloheptadiene^[172]. Thus the extraordinary reactivity of the nitroacetylene system is clearly demonstrated, even in (38) where it is most unfavourably shielded by the tert-butyl group.

8. Attempts at Cyclobutadiene Synthesis : Reaction of tert-Butyl-nitroacetylene with Ynamines^[5, 6].

Cyclobutadienes, without significantly changed electronic system, have been detected only indirectly^[179]. Some stable derivatives, however, have been prepared. One sort is exemplified by biphenylene (59) or the naphthalene derivative^[180] (60) :



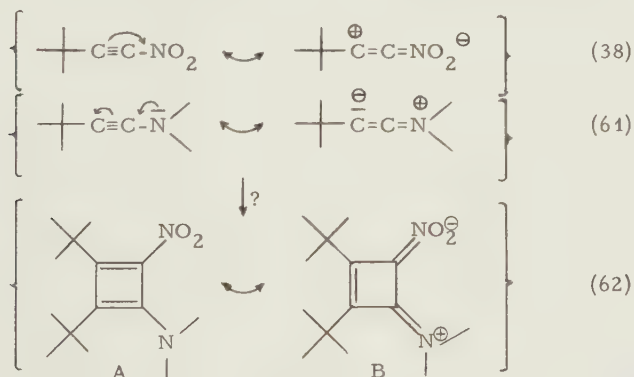
Another sort of derivatives has been obtained by the acid-induced "dimerization" of suitable substituted ynamines to cyclobutenecyanines^[173-175] and subsequent HX elimination to push-pull stabilized cyclobutadienes.



In the above cases the systems are stable because the structures drawn are not the sole, or even the principal resonance form.

These compounds may also be considered to be derivatives of the rather stable dimethylenecyclobutanes.

The inverse polarizations of the nitroacetylene and ynamine system with tert-butyl substituents promised a direct combination to the cyclobutadiene system. In the resulting nitroenamine unit, the push-pull effect should be maximized^[181-182] and thus contribute in an appreciable manner to the non-cyclobutadiene resonance form (62B). Attempts at cyclobutadiene synthesis applying the nitroenamine group as push-pull system have been carried out especially by Breslow and coworkers, but the results were negative^[182, 183].



[179] For example

a) G. Maier, Communication at the GdCh meeting, Hamburg, Sept. 1969 ;

b) G. Maier and U. Mende, Tetrahedron Letters 1969, 3155.

[180] M.P. Cava, B. Hwang and J.P. van Meter, J. Amer. Chem. Soc. 85, 4032 (1963).

[181] S.L. Manatt and J.D. Roberts, J. Org. Chem. 24, 1336 (1959).

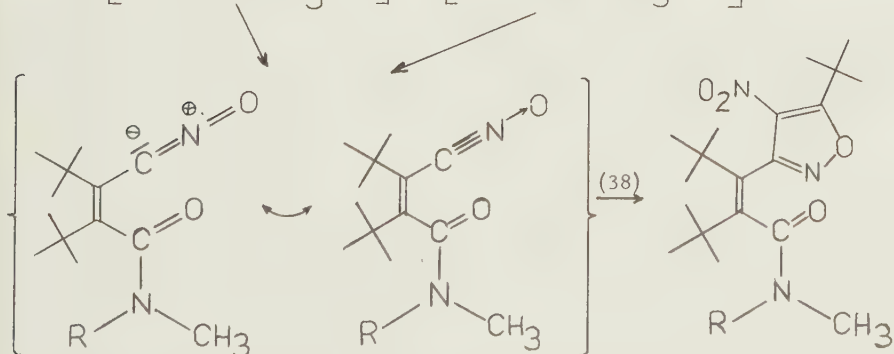
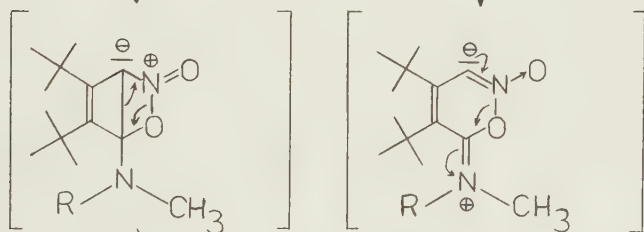
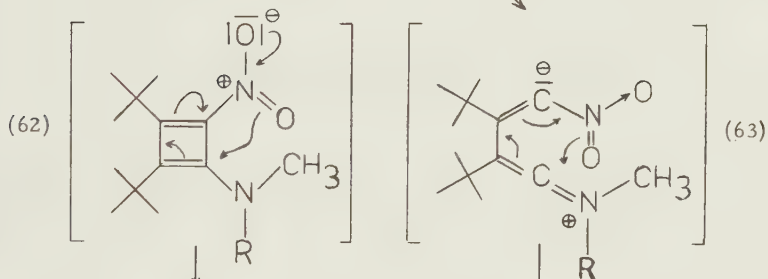
The stability of compounds as (62) having the further advantage of steric stabilization by the bulky tert-butyl groups, was expected to permit trapping or even isolation at low temperatures.

a) Formation of 1:1 and 1:2 adducts from tert-butyl nitroacetylenes and tert-butylamines.

Indeed (38) and (61a) reacted at 0° in dry ether to give a colourless crystalline 1:1 adduct. However, this showed no longer an intact nitro group in the IR spectrum (see fig. 28). Instead a strong band at 2280 cm^{-1} had appeared. Together with the presence of a medium band at 1338 cm^{-1} [184] and a strong amide carbonyl absorption at 1642 cm^{-1} this suggested structure (64a) for the 1:1 adduct. Formation of a new C-C bond and transfer of one oxygen atom from the nitro group to the former ynamine unit had produced a nitrile oxide and an amide group (see reaction scheme).

-
- [182] R. Breslow, D. Kiselevich, M.J. Mitchell, W. Fabian and K. Wendel, J. Amer. Chem. Soc. 87, 5132 (1965).
- [183] For unsuccessful approaches to the cyclobutadienes, see also M.P. Cava and M.J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York-London 1967.
- [184] IR spectra of stable aromatic nitrile oxides : S. Califano, R. Moccia, R. Scarpati and G. Speroni, J. Chem. Physics 22, 1777 (1957).

Reaction scheme, formation of 1:1 and 2:1 adducts from (38) and (61).



(64)

(65)

(61), (64), (65) : (a) R = CH₃, (b) R = C₆H₅

According to infrared spectra the reaction of (38) with (61a) to afford (64a) was quantitative, but (64a) decomposed partially on recrystallization and was isolated in 29% yield only. Similarly, the corresponding nitrile oxide (64b) derived from N-methyl-N-phenyl-tert-butylnamine, was isolated from the reaction of (38) and (61b), ratio 1:1^[185] in 21% yield. In addition, a 2:1 adduct (65b) was isolated from this reaction mixture. (65b), an isoxazole derivative, was formed in the competitive reaction of the originally formed nitrile oxide (64b) with the nitroacetylene (38) by a 1, 3-dipolar cycloaddition (see also B-IV/9).

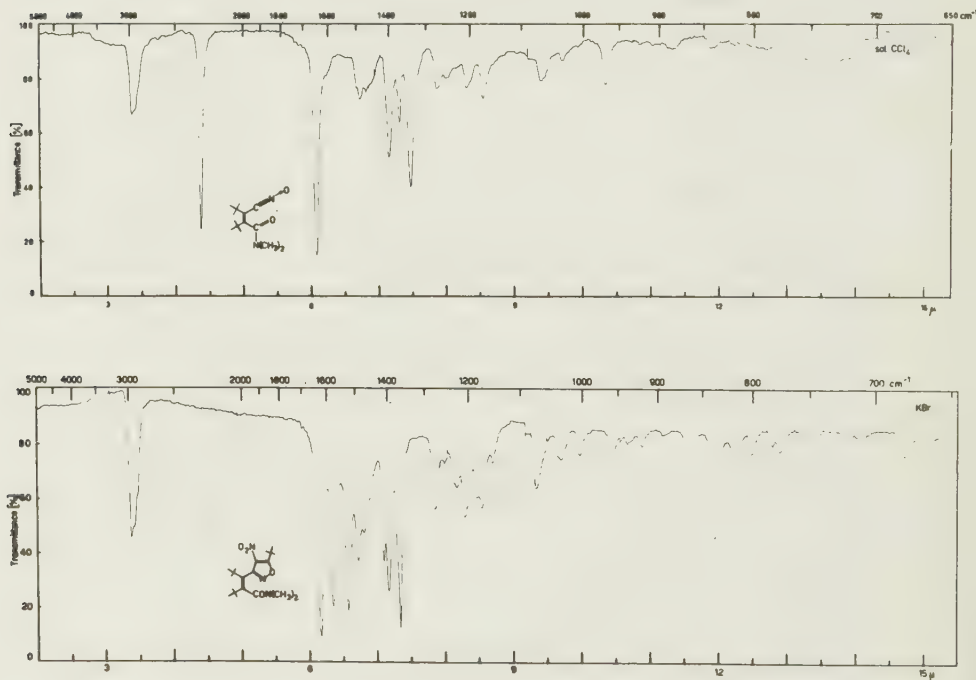


Fig. 28. IR spectra of the 1:1 adduct (64a) and of the 2:1 adduct (65a).

The analogous product (65a) could be obtained from (61a) with excess nitroacetylene (38). The low yield of isolated product (44%) here was due to the enhanced solubility of (65a) even in hydrocarbon solvents. The IR spectra of (64a) and (65a) are given in figure 28, the UV spectra of (64b) and (65b) are represented in figs. 29 and 30, resp..

In order to detect intermediates such as the cyclobutadiene derivative (62) or the acyclic dipole (63), the nitroacetylene (38) and the tert-butylamine (61a) were mixed in a 1:2 ratio at -60° in a NMR tube. On warming to -30° the reaction started. However, no peaks other than those deriving from the independently isolated 1:1 and 2:1 adducts (64a) and (65a), resp., could be observed. Moreover, from phenylacetylene solutions of (38) and (61a), ratio 1:1, only the isoxazole (69a) was produced. (69a) was formed in a 1,3-dipolar addition of the intermediate 1:1 adduct, the nitrile oxide (64a), with phenylacetylene (see also the following paragraph B-IV/9). This corresponds exactly to the formation of the 2:1 adducts (65) mentioned before. The above reactions are summarized in the scheme on p. 129.

N,N-Diethyl methyl- and phenylamine probably reacted with (38) in the same way as (61a) and (61b). Infrared spectra taken immediately after addition of (38) to the ynamine solutions at 0° showed rapidly diminishing absorptions at 2280 cm^{-1} corresponding to analogous nitrile oxides. Comparing models of these nitrile oxides with those isolated, i.e. (65a) and (65b), resp., indicated less efficient steric protection of the nitrile oxide group. No efforts were made to isolate products from these reactions.

[185] (64b) was isolated in 66% yield when the nitroacetylene (38) and the ynamine (61b) were reacted in a 1:4 ratio.

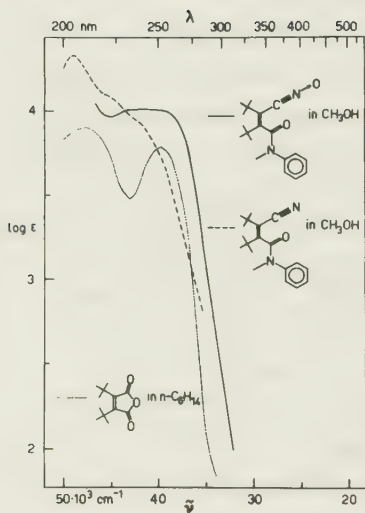


Fig. 29. UV spectra of a 1:1 adduct, the nitrile oxide (64b) and degradation products, the nitrile amide (66b) and di-tert-butylmaleic acid anhydride (67).

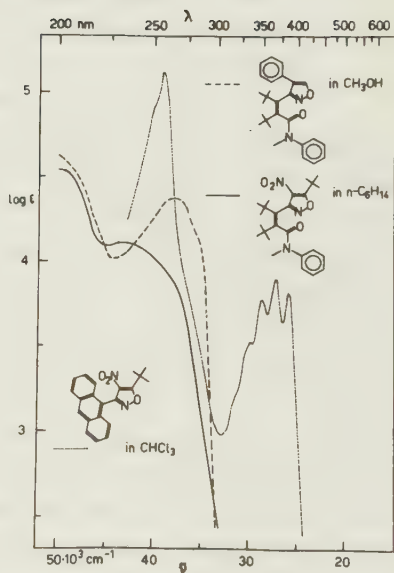
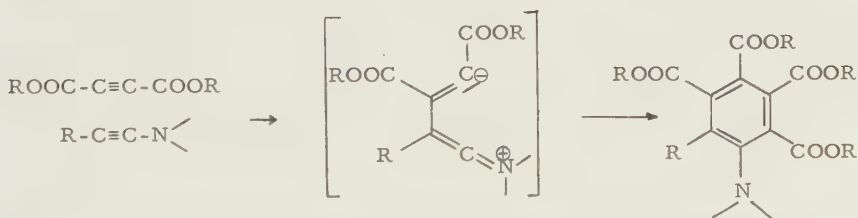
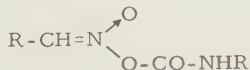


Fig. 30. UV spectra of some isoxazoles : the 2:1 adduct (65b); (69b), the product from phenylacetylene and the 1:1 adduct (64b); (71), the adduct of the nitroacetylene (38) with 9-anthracene-fulmide.

The reaction of tert-butylnitroacetylene (38) with ynamines is in contrast to the reactions of other electrophile acetylenes such as acetylene dicarboxylates with ynamines. In the latter reactions only 2:1 adducts have been isolated^[8, 173, 186]. This has been rationalized by the formation of an intermediate 1,4 dipole^[187] which cannot collapse to form the cyclobutadiene derivative. Another way of stabilization as encountered in the nitroacetylene-ynamine reaction, namely oxygen transfer, is not possible either. Therefore the 1,4-dipole adds another dipolarophile to afford the stable benzene derivative^[8, 173, 186];



Oxygen abstraction from aliphatic nitro groups to give nitrile oxides has been reported previously^[188]. Nitroalkanes of the general formula $\text{R}-\text{CH}_2-\text{NO}_2$ eliminate water when treated with isocyanates and triethylamine. Apparently the reaction proceeds via the mixed anhydride of a nitronic^[189] and a carbamic acid, whereas in our case the first reaction step certainly involves formation of a new C-C linkage.

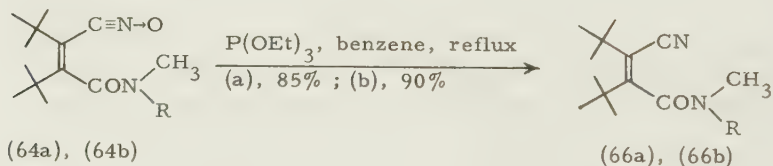


- [186] a) J. Ficini and C. Barbara, Bull. Soc. Chim. France 1964, 871 ;
 b) H.G. Viehe, R. Fuks and M. Reinstein, Angew. Chem. 76, 571 (1964) ; ibid. internat. Edit. 3, 581 (1964).

The stereochemistry of the nitrile oxides (64a) and (64b) could not be established directly (cp. the reduction products, the nitriles (66a) and (66b), discussed below). From their way of formation and their degradation to di-tert-butylmaleic acid anhydride (67), which is detailed below, it seems reasonable to assume that the tert-butyl groups are cis.

b) Degradation of the 1:1 adducts, the nitrile oxides (64a) and (64b).

The amide nitrile oxide structures (64a) and (64b) assigned to the 1:1 adducts could be confirmed by degradation. Triethylphosphite in refluxing benzene has been found by Grundmann and Frommelt to reduce nitrile oxides to the corresponding nitriles in high yields [50]. Likewise, (64a) and (64b) were converted smoothly into the di-tert-butylmaleic acid nitrile amides (66a) and (66b) :



[187] For the concept of 1,4 dipolar cycloaddition see R. Huisgen and K. Herbig, *Liebigs Ann. Chem.* **688**, 98 (1965).

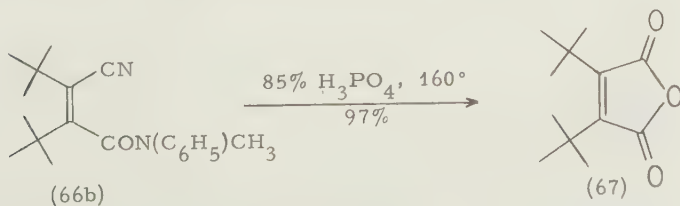
[188] T. Mukaiyama and T. Hoshino, *J. Amer. Chem. Soc.* **82**, 5339 (1960).

[189] cf. A.T. Nielsen in H. Feuer (ed.), "The Chemistry of the Nitro and Nitroso Groups", Part 1, Chapter 7 (Nitronic Acids and Esters), Interscience, New York-London-Sydney-Toronto, 1969.

(66a) and (66b) showed IR spectra resembling those of (64a) and (64b), apart from the two missing nitrile oxide absorption bands. New weak bands of the nitrile stretching vibrations appeared at 2230 and 2205 cm^{-1} , resp.. The IR spectrum of (66b) is given in fig. 31, its UV spectrum is seen in fig. 29. on page 132.

The configuration of the nitriles (66) is assumed to be that with cis tert-butyl groups, i.e. analogous to the nitrile oxides (64). The NMR spectrum of the nitrile oxide (64b), the phenyl derivative, had revealed the presence of 11% of a second isomer. Similarly, the phenyl derivative (66b) isomerized slowly in CDCl_3 solution, as was followed by NMR spectroscopy. However, after 10 days, the resulting mixture showed still 56% of the starting isomer. The other nitrile with the N,N-dimethylamino group did not isomerize under the same conditions. Neither addition of iodine nor heating to 95% in CCl_4 solution for one week gave rise to changes in its NMR spectrum. An unambiguous configurational assignment by NMR means thus was not possible.

However, the view of cis tert-butyl groups in the original 1:1 adducts was supported by the hydrolysis of (66b). While heating (66b) with KOH in glycol yielded mixtures, the acid hydrolysis with conc. phosphoric acid^[190] provided di-tert-butyl maleic acid anhydride (67) in almost quantitative yield :



[190] Cp. Houben-Weyl, VIII/3, p. 431 (1952).

The structure of (67) was established by the usual means. Its NMR spectrum shows a single peak at 1.49 ppm due to the tert-butyl protons. In its IR spectrum, given in fig. 31, the carbonyl absorptions appear at 1830 and 1755 cm^{-1} . Maleic acid anhydrides are known to absorb at 1835-1810 and 1770-1760 cm^{-1} [191]. As to be expected of a symmetric molecule, the IR C=C stretching frequency at 1628 cm^{-1} appears with very low intensity.

The UV and the mass spectrum of (67) are represented in figs. 29 and 32, resp. The expected fragment corresponding to di-tert-butylacetylene at $m/e = 138$ appears very weak. Its formation is supported by metastable analysis. The loss of methyl groups from the parent ion is preferred.

(67) represents one of the rare cyclic compounds with 1,2-di-tert-butyl groups [192]. A model consideration indicates extreme steric crowding of the cis tert-butyl groups. Fumaric acid can be transformed into maleic acid anhydride only by prolonged heating to 140° with a dehydrating agent, acetyl chloride [193]. The di-tert-butyl compound should be energetically highly unfavoured so that the anhydridisation of a di-tert-butylfumaric acid derivative should require much higher temperatures. The smooth hydrolysis and cyclization described above therefore may be taken as evidence for the cis-di-tert-butyl arrangement of the nitrile oxides (64) isolated from the reaction of tert-butyl nitroacetylene (38) with the tert-butylamines (61).

[191] A.R. Katritzky and A.P. Ambler in "Physical Methods in Heterocyclic Chemistry", Vol. 2, Academic Press, New York-London 1963, p. 191.

[192] For benzene derivatives with ortho tert-butyl groups, see [173] and U. Kruerke, C. Hoogzand and W. Hubel, Chem. Ber. 96, 2817 (1961), and C. Hoogzand and W. Hubel, Tetrahedron Letters, 1961, 637.

[193] loc. cit. [83a], p. 106 f.

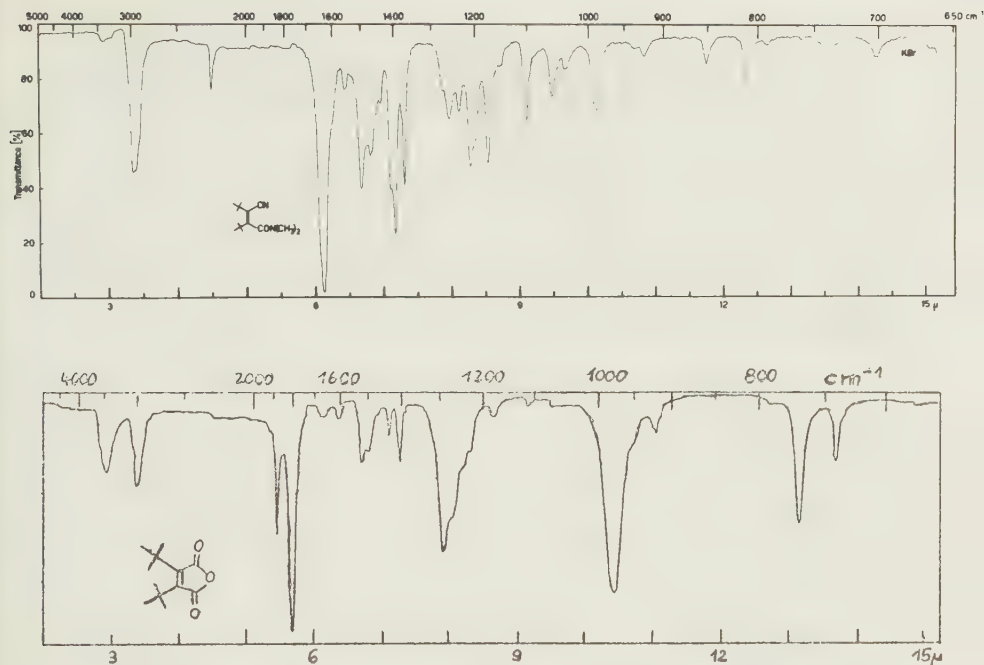


Fig. 31. IR spectra of the degradation products from the 1:1 adducts (64), the nitrile amide (66b) and the di-tert-butylmaleic acid anhydride (67).

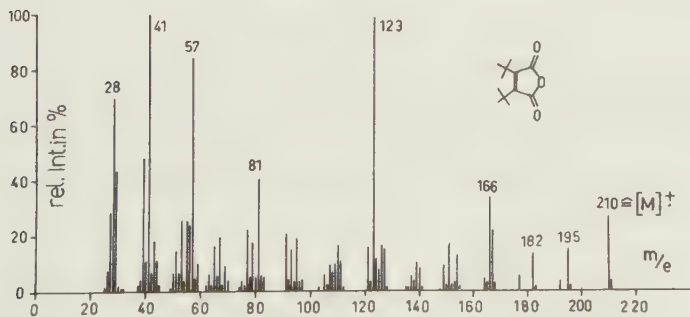


Fig. 32. Mass spectrum of di-tert-butylmaleic acid anhydride (67).

9. 1,3-Dipolar Additions of the 1:1 Adducts, the Nitrile Oxides (64);
Reaction of Tert-Butylnitroacetylene with 1,3 Dipoles^[6]

The first 1,3 dipolar cycloaddition of nitroacetylenes was encountered in the reaction with ynamines where 1,2 cycloaddition to cyclobutadienes was expected to occur. This was the subject of the preceding paragraph. The 1:1 adducts isolated from this reaction represent stable unsaturated nitrile oxides.

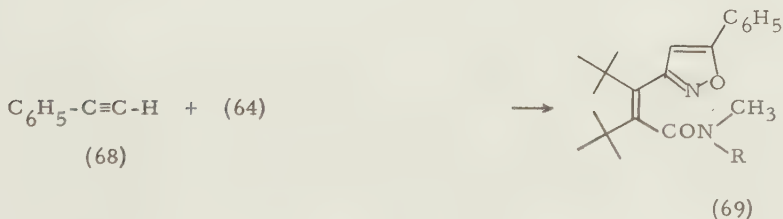
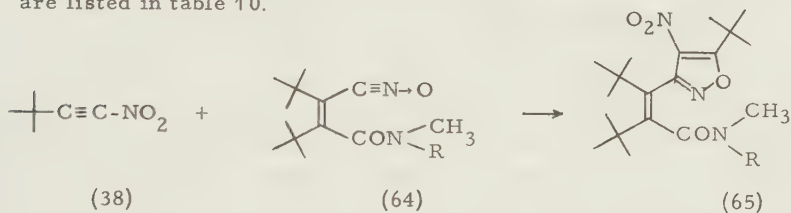
The synthesis of the first perfectly stable aliphatic saturated and unsaturated nitrile oxides has been published recently by C. Grundmann and S. K. Datta^[30b]. From the limited lifetime of the tert-butyl substituted nitrile oxide^[53a, 194] it was concluded^[30b] that bulkier groups such as di-tert-butylmethyl or 2,6,6-trimethyl-cyclohexen-1-yl should render nitrile oxides stable isolable compounds. Indeed, it has been found that the dimerization of these fulmides to furoxans is completely inhibited at room temperature^[30b]. Nevertheless, 1,3 dipolar addition products with phenylacetylene have been obtained in high yields^[30b].

Likewise, the stable unsaturated nitrile oxides formed from tert-butylnitroacetylene and tert-butylnamines contain bulky substituents. The N-methyl-N-phenyl derivative (64b) proved more stable than the N,N-dimethyl compound (64a) which decomposed slowly when stored at room temperature. In spite of their voluminous substituents, (64a) and (64b) underwent normal 1,3-dipolar cycloadditions similar to the statements of Grundmann et al. concerning stable aliphatic and aromatic nitrile oxides^[30b, 195].

[194] a) G. Zinner and H. Günther, *Angew. Chem.* 76, 440 (1964); *ibid.* *internat. Edit.* 3, 383 (1964).

b) G. Speroni and A. Quilico in A. Weissberger (ed.), "The Chemistry of Heterocyclic Compounds", Vol. 17, Interscience, New York, 1961, p. 21 f.

The addition of the nitroacetylene (38) to the 1:1 adducts (64a) and (64b) to produce 2:1 nitroacetylene-ynamine adducts has already been demonstrated in the preceding paragraph. Likewise, the 1:1 adducts (64) with phenylacetylene (68) at room temperature gave the corresponding isoxazoles (69). A stable aromatic nitrile oxide, 9-anthracene-fulmide^[196] (70), reacted similarly with tert-butyl nitroacetylene (38). The IR spectrum of the isoxazole (65a) is given in fig. 28, p. 130, the UV spectra of (65b), (69b) (adduct from (64b) and phenylacetylene), and of (71) (adduct from (38) and (70)), are seen in fig. 30, p. 132. The yields of isoxazoles obtained are listed in table 10.



[195] For the similar behaviour of stable aromatic and heterocyclic nitrile oxides see

- a) C. Grundmann and J. M. Dean, *J. org. Chem.* 30, 2809 (1965);
- b) C. Grundmann and R. Richter, *ibid.* 32, 2308 (1967).

[196] C. Grundmann in Houben-Weyl, X/3, 1965, p. 846.

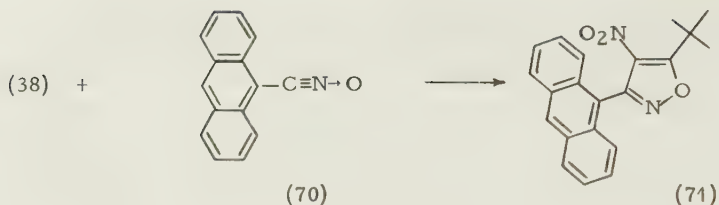


Table 10. Isoxazoles from the nitrile oxides (64a), (64b), and (70) and the nitroacetylene (38) or phenylacetylene (68).

Reactants	Product	Yield	Remarks
(38) + (61a) 2:1	(65a)	44%	nitrile oxide (64a) not isolated
(38) + (61b) 1:1	(65b)	41%	besides 21 % of (64b)
(38) + (61a) + (68)	(69a)	69%	solvent phenylacetylene (68)
(64b) + (68)	(69b)	69%	"
(38) + (70) 1:1	(71)	93%	in CHCl_3

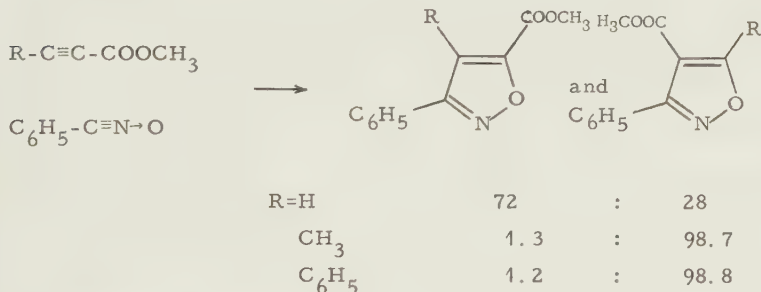
The reaction of nitrile oxides with arylacetylenes $\text{Ar}-\text{C}\equiv\text{C}-\text{H}$ recently has been shown not to proceed exclusively through a 1, 3 dipolar concerted cycloaddition^[197]. Substantial quantities $\text{R}-\text{C}\equiv\text{C}-\text{Ar}$ of open-chain acetylenic oximes have been isolated  from the residual oily mixtures after crystallization of the isoxazoles. These oximes, deriving from a competing reaction, cyclized readily to afford the isoxazoles^[197]. As the products obtained from phenylacetylene and the nitrile oxides (64) in this work, crystallized very slowly, the mother liquors also may have contained these acyclic isomers.

[197] a) S. Morrochi, A. Ricca, A. Zanarotti, G. Bianchi, R. Gandolfi and P. Grünanger, *Tetrahedron Letters* **1969**, 3329.

b) A. Battaglia and A. Dondoni, *ibid.* **1970**, 1221.

Similarly, only one of the two possible spatial isomers could be isolated here. The orientation of substituents, as it is represented in (69) for the phenylacetylene case, is concluded according to literature results^[30b, 53a, 173, 195, 197-200] and discussions^[201].

Christl and Huisgen reported the direction of benzonitrile oxide additions to acetylene carboxylates to be determined by the substituent R of the acetylenic carbon^[200]:



[198] For reviews on 1,3 dipolar cycloadditions see

a) loc. cit. ^[173]

b) R. Huisgen, R. Grashey, and J. Sauer in S. Patai (ed.), "The Chemistry of the Alkenes", Wiley-Interscience, New York, 1964, p. 379.

c) R. Huisgen, Angew. Chem. 75, 604 (1963); *ibid.* *internat. Edit.* 2, 565 (1963); Angew. Chem. 75, 741 (1963); *ibid.* *internat. Edit.* 2, 633 (1963).

[199] G. Lovecchio and P. Monforte, Gazz. chim. ital. 86, 399 (1956).

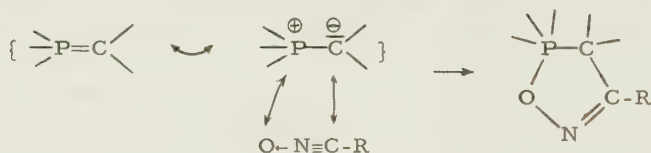
[200] M. Christl and R. Huisgen, Tetrahedron Letters 1968, 5209.

[201] For a recent discussion of the mechanism of 1,3 dipolar cycloadditions, see

a) R. A. Firestone, J. org. Chem. 33, 2285 (1968);

b) Reply: R. Huisgen, *ibid.* 33, 2291 (1968).

In analogy the isoxazoles obtained from tert-butyl nitroacetylene (38) should have their substituents oriented as seen from formulas (65) and (71). This corresponds also to the polarization in the nitroacetylene (38) and nitrile oxides. 1,3 Dipoles have a system of 4 π electrons and three atoms with p-orbitals available (allyl anion type). Nevertheless, in part due to its greater electronegativity, the oxygen atom of a $-C\equiv N\rightarrow O$ group bears a partial negative charge. Thus, it seems reasonable that this oxygen atom in the above concerted cycloadditions combines with the positivized β -carbon of the nitroacetylene. Analogous orientation corresponding to the charge distribution in the reactants has been observed when alkylidenephosphoranes were reacted with nitrile oxides^[202]:



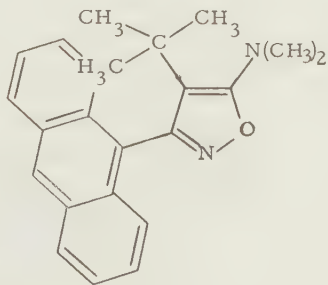
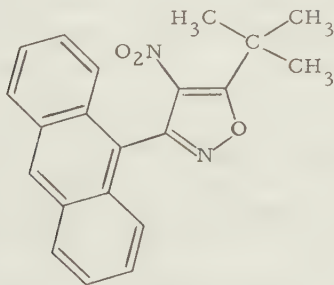
In the reaction of tert-butyl nitroacetylene (38) with tert-butylamines (61) the intermediate nitrile oxide might have reacted further with both of these dipolarophiles. Ynamines are known to provide high yields of adducts with 1,3 dipoles^[203]. However, the results of the above reaction indicated that the nitroacetylene reacted faster towards nitrile oxides. This was confirmed more quantitatively. (38) and the tert-butylamine (61a) separately were allowed to react in a 1:1 ratio with anthracen-9-fulmide in benzene and the reactions followed by IR spectroscopy. The

-
- [202] a) R. Kunstmann, Dissertation Univ. Erlangen-Nürnberg 1968;
 b) H. J. Bestmann and R. Kunstmann, Chem. Ber. 102, 1816 (1969);
 c) R. Huisgen and J. Wulff, *ibid.* 102, 1833 (1969).
- [203] R. Fuks, R. Buijle, and H. G. Viehe, Angew. Chem. 78, 594 (1966);
ibid. internat. Edit. 5, 585 (1966).

nitroacetylene (38) had disappeared almost completely after 3 hours, whereas the ynamine concentration had only slightly diminished. (61a) reacted at least 10 times more slowly. The corresponding adduct from (61a) was not characterized due to lack of time.

Nitrile oxides are electron-rich 1,3 dipoles. Therefore they should be expected to react faster with electrophiles than with nucleophiles, provided that the substituents employed are of comparable size and nature. From electron-poor 1,3 dipoles, the inverse should be expected. Indeed, it was found that relatively electrophilic 1,3 dipoles such as phenylazide reacted much faster with (61a) than with (38)^[119a]. However, a direct comparison of the 1,3 dipolarophilic reactivity of the nitroacetylene and the ynamine system by these methods is not yet possible. This would require the absence of steric interactions, i. e. nitroacetylene, ynamine and nitriloxide with smaller and thus negligible substituents such as H or CH₃. These nitroacetylenes have not yet been synthesized.

In the case of the tert-butyl derivatives (38) and (61a) unequal steric crowding in the transition states may account for the rate differences. In addition, the different reactivities of the basic systems may likewise contribute. The presumed orientation in the nitroacetylene adduct is much more favourable than that expected for the ynamine case :



10. The Nitroacetylene System in Diels-Alder Additions.

a) Reactions of Nitroacetylenes with 1, 3 Dienes.

The "Alder Rule" for usual Diels-Alder additions generalizes the findings that the rates are increased by electron-donating substituents in the diene and electron-attractive substituents in the dienophile^[204, 205]. These 1,4 cycloadditions, however, are very sensitive to steric effects. If the bulky tert-butyl group in the nitroacetylene (38) would not completely inhibit additions, it was expected to proceed best with electron-rich, alicyclic dienes.

A number of commercial or easily available dienes were allowed to react with (38) at room temperature without solvent or in solutions as concentrated as possible: 2,3-dimethyl-1,3-butadiene, cyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, cyclooctatetraene, tetracyclon, furan, 2,5-dimethylfuran, diphenylisobenzofuran. With (38), only cyclopentadiene (72), one of the most reactive dienes of the electron-rich types^[204, 205], gave a smooth addition at room temperature to yield the corresponding norbornadiene derivative (74). The reaction was followed by GLC analyses. The formation of (74) was found to be much faster than the dimerization of the diene (72). The separation of these two adducts was achieved by means of LSC on silicagel. The hydrocarbon (73) was removed from the column already by cyclohexane, the more polar

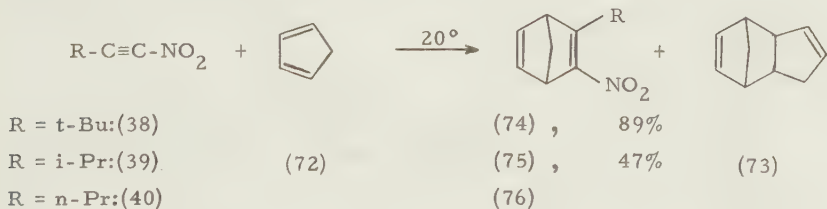
[204] K. Alder, *Experientia Suppl.* II, 86 (1955).

[205] a) Review of "New Preparative Aspects" of Diels-Alder reactions, J. Sauer, *Angew. Chem.* 78, 233 (1966); *ibid. internat. Edit.* 5, 211 (1966).
 b) "The Reaction Mechanism", J. Sauer, *Angew. Chem.* 79, 76 (1967); *ibid. internat. Edit.* 79, 76 (1967); see also ref. [173, 178, 198a].

nitroolefin (74) was eluted with benzene and obtained in high yield as a yellow liquid. (74) was oxidized on standing at the air; the analogous compounds (75) and (76) were even more air-sensitive.

Reduction of (74) by LAH and subsequent benzoxylation yielded the benzamide (78), similarly as done with tert-butylnitroacetylene (38) (B-IV/2) and the nitroenamine (47) (B-IV/6). The structure of (78) was in accord with its analytical and spectral data, confirming once more the structures of the nitroacetylene (38) and of the diene adduct (74).

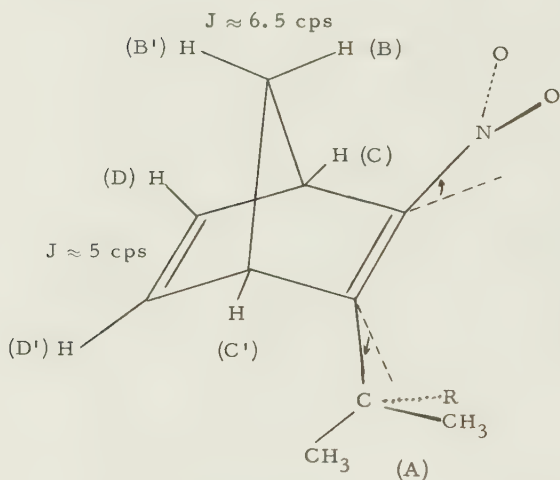
Isopropylnitroacetylene (39) and n-propylnitroacetylene (40) were shown to react similarly with cyclopentadiene (73). Owing to difficulties involved in its purification and to lack of time, the n-propyl nitronorbornadiene (76) was identified only by GLC analysis and NMR spectroscopy. The 1,3-cyclohexadiene adduct (77) from isopropylnitroacetylene isolated in very small quantity could not be characterized in a satisfactory manner.



From considerations of a model it is seen that the cis-tert-butyl-nitroolefin unit is not coplanar and full conjugation therefore is not possible. Equilibration attempts of trans-tert-butylnitroethylene^[19a, e] confirmed that this arrangement is energetically very unfavourable.

The consequences of this steric crowding, as observed from UV and IR spectra, have already been discussed for the example of the tert-butyl-iodonitroolefin (26a) in part B-I/4. The spectra of tert-butyl-nitronorbornadiene (74), compared with the less strained isopropyl derivative (75), exhibit also the characteristic differences.

The NMR spectra of (74) and (75), given in fig. 33, show similar absorption patterns for the olefinic protons. The coupling constant for the cis vinyl protons in (74) is 5 cps and thus within the normal range 4.3-6.5 cps, found from norbornenes and norbornadienes^[206].



	(74)	(75)
(A)	1.15	0.94, 1.20
(B)	2.1	2.12
(C)	3.8	3.8, 4.0
(D)	-	3.7
(E)	6.92	6.88

R = CH₃ : (74)

R = H : (75)

The positions of the vinyl and of the bridgehead protons correspond to the results reported of other norbornadienes^[206, 207].

[206] loc. cit. [16], p. 157 f.

[207] a) R. P. Gandhi and V. K. Chadha, Chem. Comm. 1968, 552;
b) D. Seyferth and J. D. H. Paetsch, J. org. Chem. 34, 1483 (1969).

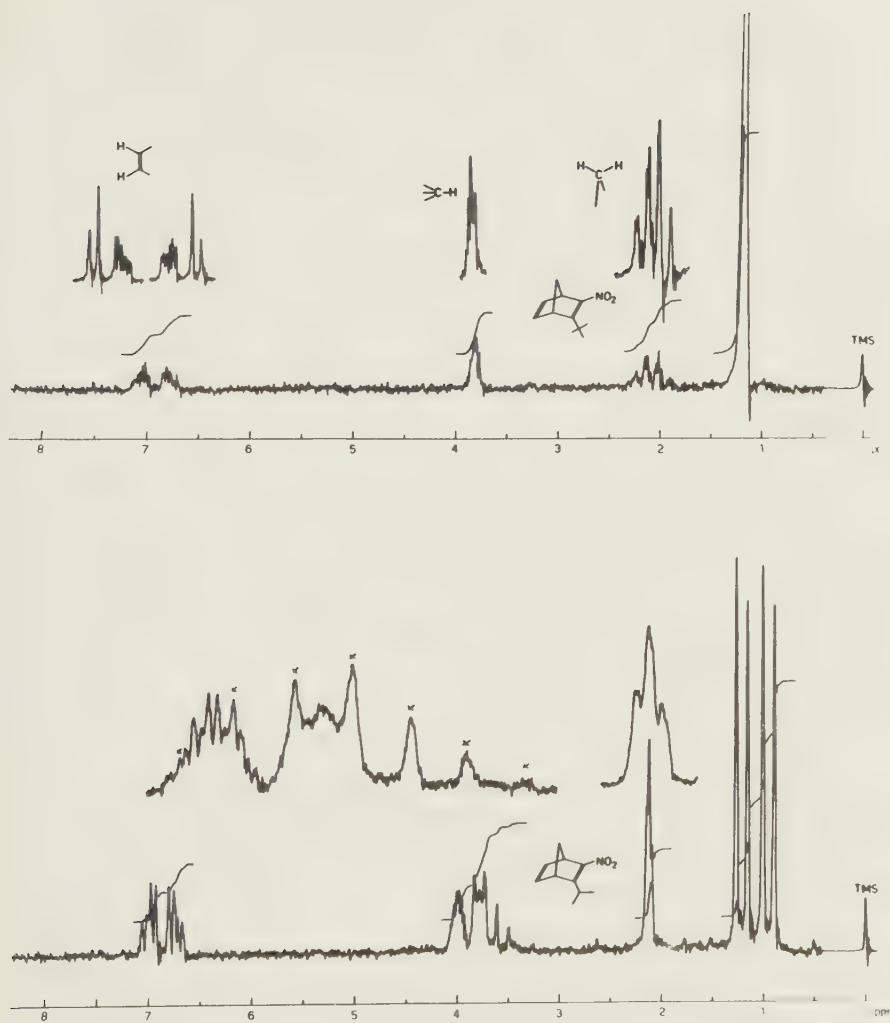


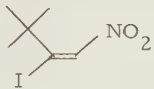
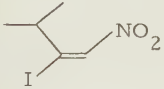
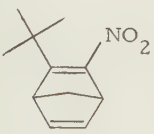
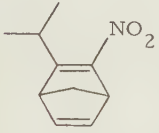
Fig. 33. NMR spectra of the nitronorbornadienes (74) and (75).

The pattern exhibited by the methylene bridge protons of (74) is completely different from that of (75). From the less strained compound (75) a slightly distorted triplet is obtained indicating a minute difference of the chemical shift of these non-equivalent protons. In (74), however, the chemical shifts of these protons (B) and (B') differ more strongly giving rise to a further split AB system. To account for the differences of (B) and (B') in (74) a distortion of the NO₂ and t-Bu groups around the C=C axis (NO₂ moving towards the bridge as indicated in the figure) or twisting of the nitro group around the C-N axis must be assumed. The anisotropic effect of the nitro group^[115b], negligible in (75), should operate on the bridge protons affecting one considerably stronger than the other.

Splitting of the usual methyl group doublet in isopropyl compounds is known to occur when a) rotation is restricted or b) the isopropyl group is neighbouring an asymmetric carbon atom^[208]. As the isopropyl group of the iodonitroolefin (27a) cis to a nitro group appears as a doublet, the splitting in the NMR spectrum of (75) probably is due to asymmetry.

Similar to the findings with iodonitroolefins (B-I/4), the most striking effect of the steric interaction of cis t-Bu and NO₂ on infra-red absorptions is observed with the C=C stretching mode of the nitroolefin unit. The IR spectra of (74) and (75) in fig. 34 and the following table illustrate this:

[208] loc. cit. [16], p. 44, 88 f.

Compound	-C=C-NO_2	
	Position	IR absorptions Intensity (transmittance)
 (26a)	1647	medium (50%)
 (27a)	1600	strong (30%)
 (74)	1590	weak-medium (65%)
 (75)	1620	strong (30%)

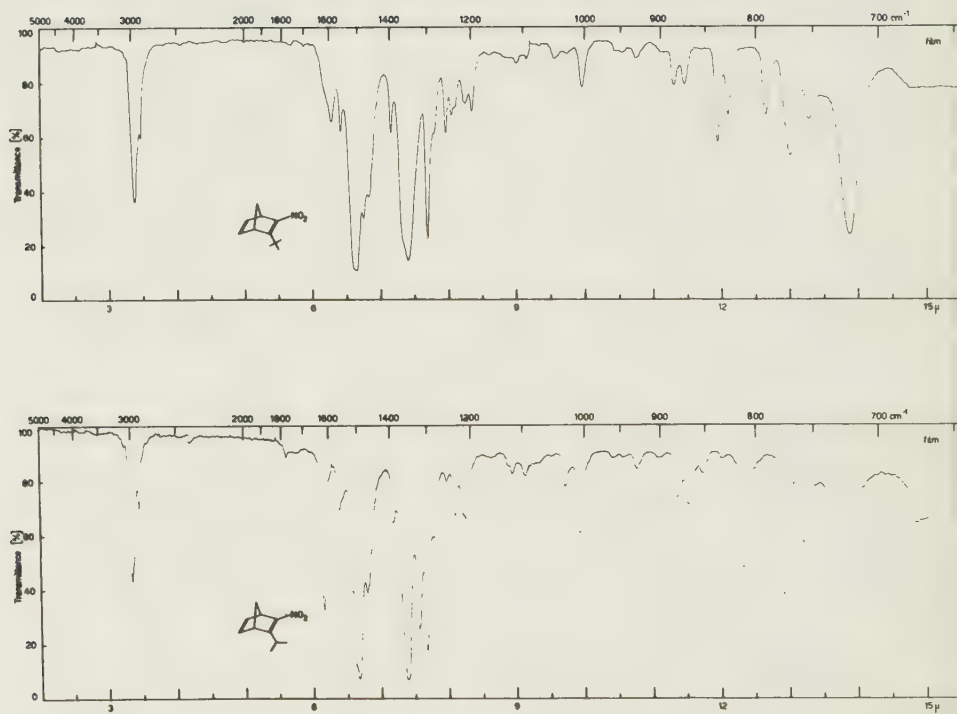


Fig. 34. IR spectra of (74) and (75).

Comparison of the electronic absorption spectra of (74) and (75) reveals also the hindered conjugation in the *t*-butyl derivative. A similar effect has been encountered with the corresponding iodonitroolefins (26a) and (27a). The UV spectra of these four nitroolefins are given in fig. 35. The absorption intensities obtained from the *tert*-butyl compounds (26a) and (74) with cis nitro group are about 50% lower than those from the less strained isopropyl derivatives (27a) and (75). The strong steric interaction of cis

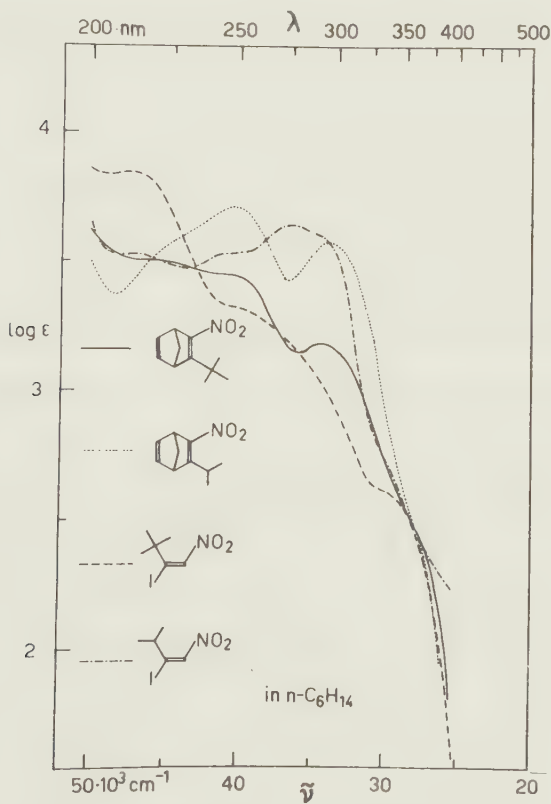
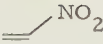
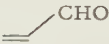
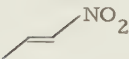
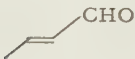
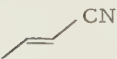


Fig. 35. UV spectra of (74) and (75), compared with those of the corresponding iodonitroolefins (26a) and (27a).

tert-butyl and nitro group in (75) is also remarked when ESR spectra of (75) and (76) are analysed^[209].

A comprehensive review about the "Diene Synthesis with Nitro Compounds" covered the literature up to 1959^[210]. Some reactions of nitroolefins with cyclopentadiene have been reported therein. Nitroethylene reacted at room temperature^[211]. When one methyl group was introduced, that is with 1-nitro-1-propene, heating to 113°^[211a] and 40-50°^[212] already was necessary yielding ca. 60% of addition product. Reactions of other straight-chain nitroolefins proceeded similarly at 100° and higher, however, no iso-propyl or tert-butyl nitroethylene apparently has been applied^[210]. To get an idea of the nitroolefins' reactivity towards cyclopentadiene, the results of some other dienophiles shall be given^[213, 210].

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- [209] A. Berndt, Univ. of Marburg, personal communication.
- [210] S. S. Novikov, G. A. Shvekgeimer, and A. A. Dudinskaya, Russ. Chem. Reviews 29, 79 (1960); cp. also ref. [212].
- [211] a) K. Alder, H. F. Rickert, and E. Windemuth, Ber. dtsch. chem. Ges. 71, 2451 (1938);
b) W. C. Wildmann and C. H. Hemminger, J. org. Chem. 17, 1641 (1952).
- [212] E. E. van Tamelen and R. J. Thiede, J. Amer. chem. Soc. 74, 2615 (1952).
- [213] H. L. Holmes, Org. Reactions 4, 60 (1948).

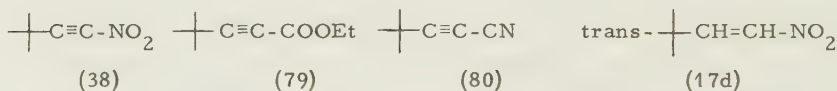
	20°	67%
	20°/24 h.	95%
	50°/3 h.	90%
	170-180°	75%
	118°/8 h.	55%
	100°/4 h.	-
	150-160°	48%

The nitroacetylene system, even with the bulky tert-butyl substituent, seems to be by far more reactive towards cyclopentadiene than the lower nitroolefin derivatives.

b) Dienophilic Reactivity of the Nitroacetylene System.

The project "nitroacetylenes" has been started because these electrophiles promised to be excellent dipolarophiles (see B-IV/8 and 9) and dienophiles. In order to get information about the relative reactivity of the new $\text{-C}\equiv\text{C-NO}_2$ system, the tert-butyl derivative (38) should be compared with other acetylenic systems whose high dienophilic reactivity is already known. Since the steric requirements should be equal, the tert-butyl compounds (79) and (80) were synthesized (see Experimental Section). A variety of trans-substituted olefins, without exception, has proven more reactive than their

acetylenic analogs^[173, 205, 214]. Therefore the corresponding nitroolefin (17d) was checked also.



Equimolar quantities of the above electrophiles were mixed with excess cyclopentadiene at room temperature and the progress of the reactions followed by GLC analysis. The nitroacetylene (38) had reacted quantitatively within 1.5-2 hours. From the other mixtures, after several days, no trace of adduct could be detected. This indicates a difference in the rate constants of at least 10^4 . It is surprising further that in the series of unsaturated nitro compounds the acetylenic system is more reactive than the corresponding nitroolefin.

From a series of trans-XCH=CHX compounds the following rate constants towards cyclopentadiene have been established^[214] indicating the relative activating efficiencies of the groups X :

trans-XCH=CHX				---C≡C-X	
COCl	COC ₆ H ₅	CN	COOMe	NO ₂	CN
≈6700	18	1.1	1.0	> 10 ⁴	1

A direct comparison of tert-butylacetylene carboxylic acid chloride with the nitroacetylene (38) should provide more quantitative information about the reactivity of the nitroacetylene system.

[214] J. Sauer, H. Wiest, and A. Mielert, Z. Naturforsch. 17b, 203 (1962).

Summary

This work deals with the synthesis and reactions of nitroacetylenes, a new class of compounds. Presumed nitroacetylenes have already been reported in 1930 and 1960. In the first part of the present work, however, it is shown that the interpretations of these previous results are wrong.

A by-product formed by the action of dinitrogen tetroxide on β -nitrostyrene in 1960 has been assigned the structure of p-nitrophenyl-nitroacetylene. The present work demonstrates that no nitroacetylene is present. Spectral data and degradation provide evidence for the heterocyclic structure of the compound in question: this has to be considered as the 3-nitro derivative of the barely known 2-azachromones (4H-1, 2-benzoxazin-4-ones).

In the other case, when hydrogen bromide is eliminated of 1-bromo-1-nitroolefins by means of primary and secondary amines, mixtures are obtained. IR spectroscopic control of these reactions shows no triple bond absorption at any time. Further attempts at nitroacetylene synthesis starting with 1-bromo-1-nitroolefins, under varying conditions met with no success. Apparently the first reaction step is addition of the base rather than deprotonation.

The configurations of the bromonitroolefins prepared and the conformations of their educts, dibromonitroethanes, are established by spectroscopic means. 3,3-Dimethyl-1,2-dibromo-1-nitrobutane exhibits a phenomenon known on similar compounds, but not yet understood. In the n-propyl and phenyl compounds only one rotamer can be detected at room temperature. In the t-butyl derivative, however, one of the rotamers by far less favourable, is present at room temperature in a 1:2 ratio.

After the failure to prepare nitroacetylenes from 1-bromo-1-nitroolefins the suitability of 2-halo-1-nitroolefins as potential nitroacetylene precursors is checked. NMR-spectroscopic findings deriving from my Diploma Thesis suggested the HX elimination of 2-halo-1-nitroolefins to be more favourable. A method reported for the NO_2 -iodine addition to phenylacetylene is applied analogously to alkylacetylenes. The resulting 2-iodo-1-nitroolefins consist of stereoisomeric mixtures. The configurations of the separated isomers are established by several independent methods. The isomer ratio of the iodonitroolefins $\text{R}-\text{CI}=\text{CH}-\text{NO}_2$ depends on the alkyl substituent R (R= Ph, t-Bu, i-Pr, n-Pr). It is rationalized considering the mechanism and nitrovinyl radical intermediates of this reaction.

Hydrogen iodide elimination, on distilling the above tert-butyl mixture over heated potassium hydroxide, affords tert-butyl-nitroacetylene. This represents the first authentic derivative of its class. The structure of this nitroacetylene is established by its spectral data, reduction and addition reactions. Other pure nitroacetylenes isolated are the i-propyl and n-propyl compound. The existence of the analogous n-butyl and phenyl compounds is proven by spectroscopic means.

As to be expected from their high ground state energy, the thermal stability of nitroacetylenes is limited. Nevertheless, their isolation is possible. Nitroacetylenes are sufficiently reactive to undergo a variety of addition and cycloaddition reactions already at or below room temperature. These reactions were mostly carried out with tert-butyl-nitroacetylene, the most stable compound of this class known up to date.

Bromine as well as water, alcohols, hydrogen chloride, primary and secondary amines smoothly add to the strongly electrophilic nitroacetylenic triple bond. These additions proceed in a directional and stereospecific manner. Further, nitroacetylenes prove excellent partners in cycloadditions with electron-rich multiple bond systems. With enamines, for example, a chain expansion by a C_2 unit results. This is detailed in the case of 1-pyrrolidinocyclopenten, where ring extension leads to a nitrocycloheptadienamine derivative.

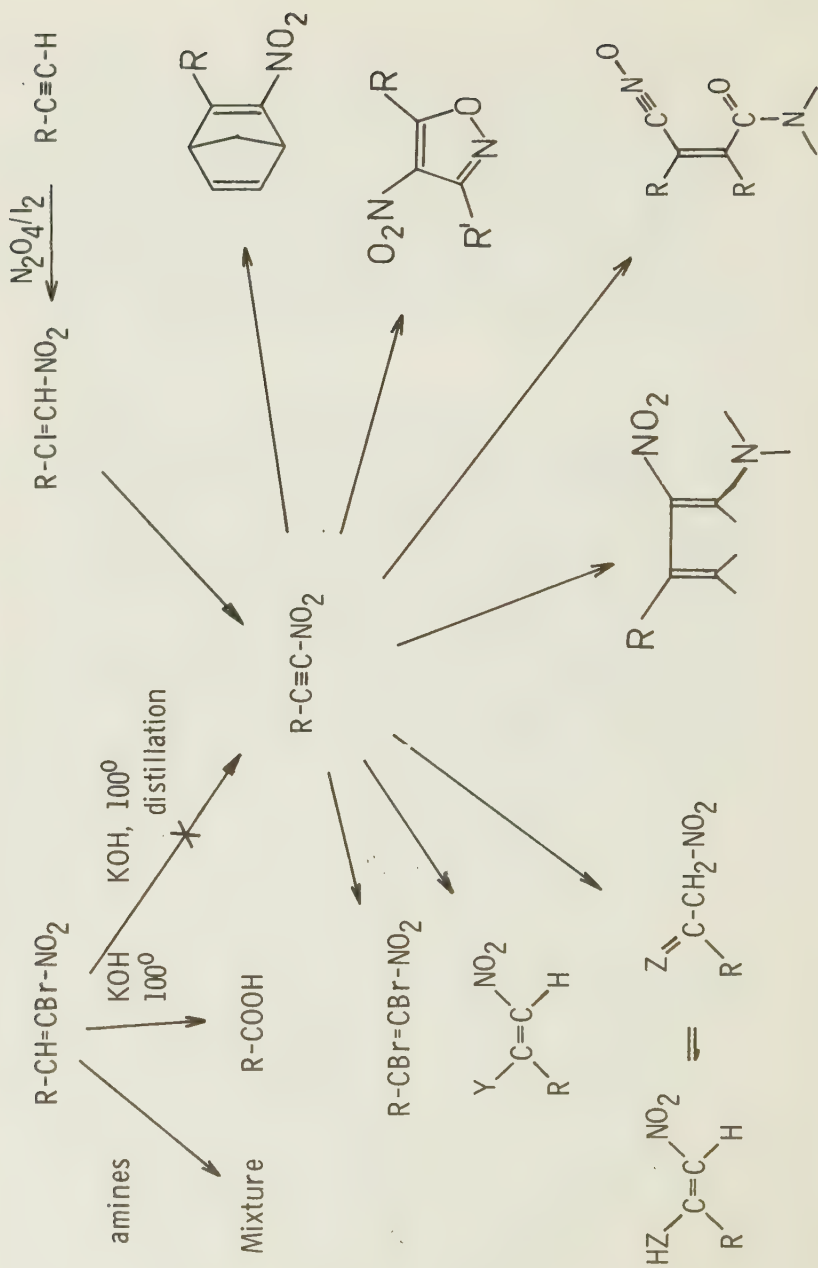
The reaction of tert-butyl nitroacetylene with tert-butylnamines is a potential one-step synthesis of push-pull substituted cyclobutadienes. In fact, 1:1 and 2:1 adducts are obtained. The former are characterized as nitrile oxide amides produced by formation of a new C-C linkage and intramolecular oxygen transfer. The 2:1 adducts are isoxazole derivatives. They derive from the subsequent reaction of the above nitrile oxides with tert-butyl nitroacetylene, which competes with the ynamine-nitroacetylene reaction. Isoxazoles are obtained also by 1,3-dipolar cycloadditions of the above nitrile oxides to phenylacetylene. No intermediate cyclobutadienes or 1,4 dipoles can be trapped. The structure of the 1:1 adducts is further confirmed by their degradation. Reduction to nitriles and hydrolysis followed by cyclization lead to di-tert-butylmaleic acid anhydride.

The dienophilic reactivity of the nitroacetylene system towards nitrile oxides is compared to that of the ynamine system by qualitative and quantitative tests.

The combination of nitro group with CC triple bond represents one of the strongest electrophile acetylenic systems. This is clear from Diels-Alder additions with cyclopentadiene. In contrast to unsaturated compounds with other electron-acceptor substituents the nitro series shows higher reactivity of the acetylene rather than of the olefin system. Similarly, the superior reactivity of the nitroacetylene is observed when compared with other tert-butylacetylenes bearing an ester or a nitrile group.

The thermal stability of nitroacetylenes decreases rapidly when passing from the t-butyl to the i-propyl and further to the n-propyl compound. This fact limits the scope of the synthetic method described here. The chemistry of nitroacetylenes has just started. This work treats only a small part of their possible reactions. New and novel reactions of nitroacetylenes remain still unexplored. However, the future preparative usefulness of nitroacetylenes depends on new synthetic routes enabling low temperature "in situ" reactions.

Nitroacetylene, Synthesis & Reaction Scheme.



Zusammenfassung

In der vorliegenden Arbeit wird über Synthese und Reaktionen von Nitroacetylenen, einer neuen Verbindungsklasse, berichtet. Vermeintliche Nitroacetylene wurden 1930 und 1960 in der Literatur beschrieben. Im ersten Teil dieser Arbeit wird gezeigt, dass diese früheren Formulierungen falsch sind. Einem Nebenprodukt, das bei der Einwirkung von Distickstofftetroxid auf β -Nitrostyrol gebildet wird, war 1960 die Struktur des p-Nitrophenylnitroacetyls zuge-schrieben worden. Aus den Ergebnissen der vorliegenden Arbeit geht hervor, dass kein Nitroacetylen vorliegt. Spektroskopische Daten und chemischer Abbau beweisen, dass diese Verbindung stattdessen als das 3-Nitro-derivat der kaum bekannten 2-Azachromone (4H-1,2-Benzoxazin-4-one) aufzufassen ist. In dem anderen Fall führt die Bromwasserstoffabspaltung aus 1-Brom-1-nitroolefinen mittels primärer und sekundärer Amine nicht zu einheitlichen Produkten: es werden Gemische erhalten; die IR-spektroskopische Kontrolle dieser Reaktionen ergibt, dass keine Dreifachbindung gebildet wird. Weitere eigene Versuche, unter den verschiedensten Bedingungen aus 1-Brom-1-nitroolefinen zu Nitroacetylenen zu gelangen, bleiben ebenfalls erfolglos. Die Basenaddition scheint gegenüber der Deprotonierung als erster Schritt begünstigt.

Die Konfiguration der dargestellten Bromnitroolefine und die Konformationen der Vorprodukte, der Dibromnitroäthane, werden spektroskopisch ermittelt. Ein von ähnlichen Verbindungen bekanntes, bisher ungeklärtes Phänomen tritt bei 3,3-Dimethyl-1,2-dibrom-1-nitrobutan auf: eines der sterisch anscheinend bei weitem ungünstigsten Konformeren, die von der n-Propyl- und Phenylverbindung nicht nachgewiesen werden können, bildet bei Raumtemperatur ein Drittel des Rotamerengleichgewichts.

Nachdem die HBr-Abspaltung von 1-Brom-1-nitroolefinen zu Nitroacetylenen gescheitert ist, werden 2-Halogennitroolefine als potentielle Ausgangsverbindungen für Nitroacetylene untersucht. Aufgrund NMR- spektroskopischer Befunde, die auf meine Diplomarbeit zurückgehen, erschien die HX-Abspaltung aus diesen Verbindungen gegenüber der HX-Eliminierung aus den stellungsisomeren 1-Halogen-1-nitroolefinen begünstigt. Eine für die Darstellung des Phenylderivates in der Literatur beschriebene Methode, die Anlagerung von NO_2 und Jod an Phenylacetylen, wird auf Alkylacetylene übertragen. Die resultierenden 2-Jod-1-nitroolefine liegen als Gemische von Isomeren vor, die getrennt und deren Konfigurationen durch verschiedene Methoden zugeordnet werden. Das Isomerenverhältnis der Jodnitroolefine R-CJ=CH-NO_2 hängt vom Kohlenwasserstoffrest R ab ($\text{R} = \text{Ph}$, t-Bu, i-Pr, n-Bu, n-Pr) und lässt sich durch genauere Betrachtung des Reaktionsablaufs sowie der intermediären Nitrovinylradikale erklären.

Die Jodwasserstoffabspaltung aus dem tert-Butylderivat durch Destillation über erhitztes Kaliumhydroxid liefert das sterisch stabilisierte, erste authentische Derivat dieser Verbindungsklasse, tert-Butyl-nitroacetylen. Die Struktur dieses Nitroacetylen wird an Hand seiner Spektraldaten, durch Reduktion und Additionsreaktionen gesichert. An weiteren Nitroacetylenen werden das i-Propyl- und das n-Propylderivat isoliert, die n-Butyl- und Phenylverbindungen spektroskopisch nachgewiesen.

Nitroacetylene sind, wie infolge ihrer hohen Grundzustandsenergie zu erwarten, thermisch begrenzt stabile, aber isolierbare Verbindungen. Sie sind so reaktionsfähig, dass sie schon bei Raum- oder tieferer Temperatur eine Reihe von Additions- und Cycloadditionsreaktionen eingehen. Diese Reaktionen werden überwiegend mit dem bisher beständigsten Nitroacetylen, der tert.-Butylverbindung, durchgeführt.

Brom sowie Wasser, Alkohole, Chlorwasserstoff, primäre und sekundäre Amine lagern sich glatt an die nitrosubstituierte, stark elektrophile Dreifachbindung an. Diese Additionen verlaufen directio- und stereospezifisch. Nitroacetylene erweisen sich weiter als ausgezeichnete Reaktionspartner in Cycloadditionen mit elektronenreichen Mehrfachbindungssystemen. Mit Enaminen, am Beispiel des 1-Pyrrolidino-cyclopenten genauer untersucht, resultiert eine Kettenverlängerung um eine C_2 -Einheit; das entspricht hier einer Ringerweiterung zu einem Nitrocycloheptadienamin-derivat.

Die Umsetzung von tert. -Butylnitroacetylen mit tert-Butylinaminen, eine denkbare einstufige Synthese für push-pull substituierte Cyclobutadiene, führt zu 1:1 und 2:1 Addukten. Erstere werden als Nitriloxid-amide charakterisiert, die durch C-C-Verknüpfung und intramolekulare Sauerstoffübertragung gebildet worden sind.

Die 2:1 Addukte der Isoxazolderivate entstammen der Folgereaktion dieser Nitriloxide mit tert. -Butylnitroacetylen, die mit der Inamin-Nitroacetylen-Reaktion konkurriert. Isoxazole werden auch durch 1,3-dipolare Cycloadditionen der obigen Nitriloxide mit Phenylacetylen erhalten. Der Nachweis intermediärer Cyclobutadiene oder 1,4-Dipole gelingt nicht.

Die Struktur der 1:1 Addukte geht auch aus dem chemischen Abbau hervor : Reduktion zu Nitrilamiden und Hydrolyse mit anschliessender Cylisierung führen zu di-tert. -Butylmaleinsäureanhydrid. Die dipolare Reaktivität des Nitroacetylensystems gegenüber Nitriloxiden wird qualitativ und quantitativ mit der von Enaminen verglichen.

Dass die Kombination von Nitrogruppe und CC-Dreifachbindung eines der stärksten elektrophilen Acetylensysteme überhaupt repräsentiert, zeigt sich in Diels-Alder Additionen mit Cyclopentadien. Im Gegensatz

zu ungesättigten Verbindungen mit anderen elektronenanziehenden Substituenten ist in der Reihe der Nitroverbindungen das Acetylen- system weitaus reaktiver als das entsprechende Olefinsystem. Der Vergleich mit anderen tert. -Butyl-substituierten Acetylenen, die eine Ester- oder Nitrilgruppe tragen, zeigt in ähnlicher Weise die überlegene Reaktivität der nitrosubstituierten Acetylenverbindung.

Die thermische Zersetzlichkeit der Nitroacetylene, die in der Reihe tert. -Butyl, Isopropyl - n-Propyl schnell ansteigt, macht die Grenzen der hier beschriebenen Darstellungsmethode deutlich. Die Chemie der Nitroacetylene steht theoretisch und experimentell am Anfang. Nur ein kleiner Teil der denkbaren Reaktionen kann in der vorliegenden Arbeit behandelt werden. Wegen der ausserordentlichen Reaktionsfähigkeit des Nitroacetylen- systems ist von den bisher dargestellten Derivaten noch eine Vielzahl neuartiger Reaktionen zu erwarten. Präparativ nützlich werden Nitroacetylene aber nur dann sein, wenn neue Syntheseprinzipien ihre Darstellung bei tiefen Temperaturen ermöglichen und sie "in situ" umgesetzt werden können.

Acknowledgements.

To all my colleagues of Dr. Viehe's former ERA team, in particular to Mr. M. Reinstein, Dr. R. Fuks, Messrs. A. Gerondal and M. Hartemink, further to Dr. C. Hoogzand, I would like to express my gratitude for steady discussions and experimental advice. I am also grateful to Dipl. Ing. R. Merényi and Mr. M. Lienart for their valuable help in recording and discussing the NMR spectra. The mass spectra were taken by Dr. F. Compennolle, Rega-Instituut Leuven, whose help in the interpretations is also acknowledged.

Chromatographic analyses were carried out by Dr. C. Moussebois, Mr. A. Delvingt, Mrs. S. Gilon and Mr. R. Houquet. IR and UV spectra were supplied by Miss C. de Meeus and Miss C. Moons. Elemental analyses were carried out by Mr. F.E. Goes and coworkers. I would like to express thanks to them for their help.

I am also indebted to Dr. W.S. Rosenberg's efforts (Univ. Louvain) to produce a not "too German" English version of this work, further to Mrs. D. Demarteau, Miss O. Stiers and Mrs. L. Fontaine for typing the manuscript.

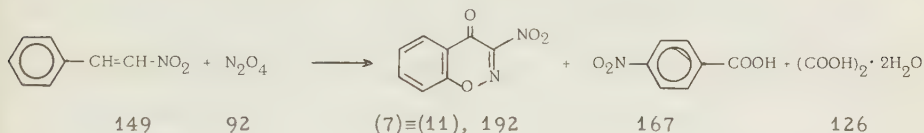
EXPERIMENTAL SECTION

Melting points were taken on a Kofler hot-stage or a Buchi "System Dr. Tottoli" apparatus. They are uncorrected. CHN analysis were carried out with an Ultramicro C.H.N-analyzer^[214] (Technicon). IR spectra were recorded on a Perkin-Elmer Model 21, UV spectra on a Cary Model 14 spectrometer. NMR spectra were obtained with a Varian A 60 spectrometer and TMS as internal standard. Chemical shifts are given in ppm with $\delta_{\text{TMS}} = 0$ ppm. The mass spectra were taken on a AEI spectrometer, model NS 12, at 70 eV. Standard GLC analysis were obtained on a F & M apparatus (conductivity detector) ; column 90 cm, 1/4" ; Chromosorb W 60-80 HMDS with 30% silicon gum ; He 60 ml/min. ; temperature program 8°/min. starting with 75°.

[215] W. Walisch, Chem. Ber. 94, 2314 (1961).

1. Structure of a Presumed p-Nitrophenylnitroacetylene^[4]

3-Nitro-2-azachromone (3-nitro-4H-1,2-benzoxazin-4-one) (11)



The reaction was essentially carried out as described by Novikov and coworkers^[3], but the products were isolated differently.

120 g (1,3 moles) of dinitrogen tetroxide was rapidly distilled into a solution of 40 g (0,268 mole) β-nitrostyrene in 150 ml of ether. The flask was fitted with an acetone-Dry Ice reflux condenser and kept at 15-16° by external cooling during a 24 h period. Another 100 g of N₂O₄ were added and the mixture kept two days at 15°. The precipitating crystals were filtered and recrystallized from chloroform-methanol yielding 0.44 g (1%) of p-nitrobenzoic acid. On cooling the solution down to -20° another crop was obtained which gave 0.56 g oxalic acid dihydrate, insoluble in chloroform. The chloroform solution was washed several times with water and provided, after evaporation of the solvent and two recrystallizations from chloroform, 1.94 g (3.8%) of 3-nitro-2-azachromone (11), yellow plates with m. p. 139-140° (Tottoli), lit.^[40, 3] 143°, 139-139.5°. The mother liquors contained still a minor amount of the azachromone (11), a larger quantity of β-nitrostyrene and at least 4 other compounds in minor quantities as shown by TLC (silicagel; ethyl acetate - cyclohexane 1:4; detection by UV 254 nm).

Analysis calc. for C₈H₄N₂O₄ :

C 50.01, H 2.10, N 14.58, O 33.31

found C 49.85, H 2.24, N 14.53, O 32.92

m.w. calc. 192.1, found 207 (osmom. in benzene).

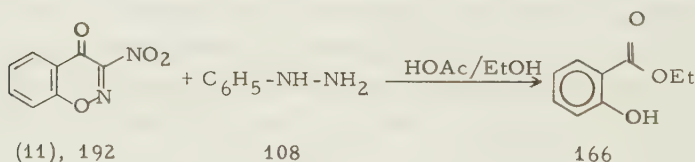
IR (KBr disk) : 1676 cm^{-1} (C=O stretch.), 1613 (aromat.), 1566 and 1550 (split asym. NO_2 stretch.), 1460 (aromat.), 1352 (sym. NO_2 stretch.), 1327 , 1040 (C-O stretch.), 771 (C-H out-of-plane def., 4 adj. H).

NMR (D_6 -DMSO) : $\delta = 7.5 - 8.4$ ppm (4H, m., aromatic). Integration was performed on an equimolar mixture of 3-nitro-2-azachromone and 1,2-dibromoethane (m.w. 188).

UV (CH_3OH) : λ_{max} 242 nm ($\lg \epsilon$ 3.90), sh 256.5 (3.83), 321.5 (3.76). In H_2SO_4 : 234 (3.86), 260.5 (3.84), 286.8 (3.88), sh 328 (3.68), 400 (3.2).

Mass spectrum : m/e 192 ($[\text{M}]^+$), 165 , 146 , 120 , 118 , 92 , 90 (base peak), 64 , 63 , 46 .

Reaction of 3-nitro-2-azachromone (11) with phenylhydrazine



According to the procedure for preparing isatine hydrazones ^[51] 108 mg (0.56 mmole) of 3-nitro-2-azachromone (11) in 20 ml of ethanol were refluxed for 12 hours with 200 mg (1.85 mmoles) of phenylhydrazine and 100 mg acetic acid. The mixture was diluted, extracted with ether, and dried with Na_2SO_4 . Removal of the solvent and bulb tube distillation gave 49 mg of a slightly yellow liquid. This product contained about 80% ethyl salicylate (yield $\approx 43\%$) which was identified by its odour, IR, NMR and GLC comparison with an authentic sample.

Alkaline hydrolysis of 3-nitro- and 3-chloro-2-azachromone (11) and (14), resp.



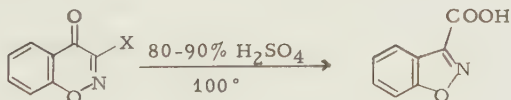
(11), X=NO₂ 192

138

(14), X=Cl 181.6

The azachromone was dissolved in 2N KOH with gentle heating, if necessary. After acidification the solution was extracted with ether, dried over CaCl₂, evaporated and recrystallized from ether-petroleum ether (b. p. 60-80°). Salicylic acid was identified by its m. p. 150-152° under subl. (lit. [216] 159°), elemental analysis and its IR spectrum. Thus 26 mg (0.135 mmole) 3-nitro-2-azachromone (11) dissolved in 3 ml 2N KOH gave 9 mg (48%), 12 mg (0.087 mmole) 3-chloro-2-azachromone (14) with 1 ml 2N KOH afforded 5.5 mg (69%) of salicylic acid.

Reaction of 3-nitro- and 3-chloro-2-azachromone (11) and (14), resp. with sulfuric acid



(11), X=NO₂ 192

163

(14), X=Cl 181.6

Solutions of 3-nitro- and 3-chloro-2-azachromone, (11) and (14), resp., were heated about 12 hours on a steam bath, until the original yellow colour had disappeared. On dilution with water, extraction with ether,

[216] Handbook of Chemistry and Physics, 49th ed. Chemical Rubber & Co., Cleveland, 1968.

removal of the solvent after drying (CaCl_2) the residue was recrystallized from ether-petroleum ether (b. p. $60-80^\circ$) to yield colourless needles, m. p. $138-140^\circ$ under dec. (reported^[52] m. p. 141°). From 102 mg (0.53 mm) of the nitro derivative (11) in 1 g of 80% H_2SO_4 36 mg (41%) of (13), from 12 mg of the chloro compound (14) in 2 g 90% H_2SO_4 6.3 mg (62%) of indoxazene-3-carboxylic acid (13) (benzisoxazol-3-carboxylic acid) were isolated.

Analysis calc. for $C_8H_5NO_3$:

C 58.90, H 3.09, N 8.59, O 29.42

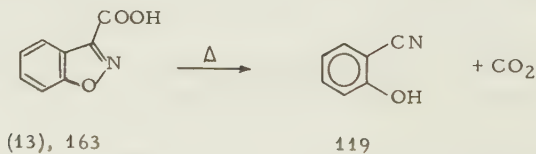
found C 58.53, H 3.34, N 8.60, O 29.38

m.w. calc. 163.1, found 152 (osm. in THF).

IR (KBr disc): 3280, 1710, 1248, 938 cm^{-1} (COOH); 1612, 1600, 1500
1453 (arom.), 756 (C-H out-of-plane def., 4 adj. H).

NMR (D_6 -acetone): δ = 8.3 - 9.0 ppm (4H, m, aromatic); 10.25 broadened (1H, COOH).

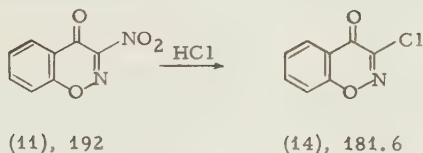
Decarboxylation of indoxazene-3-carboxylic acid^[52] (13)



6.2 mg (0.038 mmole) of indoxazene-3-carboxylic acid (13) were heated in a thick-walled test tube until no more gas evolution occurred and a colourless sublimate was obtained. This was collected by dissolving in

CHCl_3 and recrystallized (ether-petroleum ether, b. p. $60-80^\circ$) to give 3.9 mg (85%) of salicylonitrile, m. p. 94° in agreement with the literature^[216].

3-Chloro-2-azachromone (3-chloro-4H-1,2-benzoxazin-4-one) (14)



128 mg (0.667 mmole) of 3-nitro-2-aza-chromone (11) were dissolved in 5 ml CHCl_3 and ca. 300 mg HCl in 15 ml of ether-ethanol added. After about 20 hours at room temperature the IR absorptions of the nitro group at 1550 and 1352 cm^{-1} had disappeared and the solvents were evaporated leaving a colourless powder. Recrystallization from CH_2Cl_2 -petroleum ether (b. p. $60-80^\circ$) afforded 114 mg (94%) of the chloro compound (14) m. p. $107-108^\circ$ (Tottoli).

Analysis calc. for $\text{C}_8\text{H}_4\text{ClNO}_2$:

C 52.91, H 2.22, Cl 19.53, N 7.72, O 17.62

found C 52.53, H 2.28, Cl 20.00, N 7.69, O 17.53

m. w. calc. 181.6, found 170 (THF).

NMR (CDCl_3): $\delta = 7.3 - 8.3$ ppm (m; aromatic).

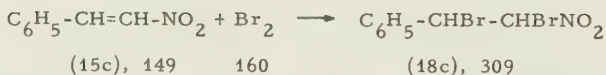
IR (KBr disc) : 1675 cm^{-1} ($\text{C}=\text{O}$ stretch.), 1612 , 1592 and 1460 (aromat.), 959 ($\text{C}-\text{O}$ vibr.), 763 ($\text{C}-\text{H}$ out-of-plane def., 4 adj. H).

UV (CH_3OH) : λ_{max} 217 nm ($\lg \epsilon$ 3.88), sh 228 (3.78), 248.5 (3.95), 255 (3.95), 278 (3.34), 322.5 (3.70). In H_2SO_4 : sh 215 (3.95), 246.6 (4.27), 261 (3.93), 316 (3.90), 383.8 (3.36).

Mass spectrum: m/e 183, 181 ($[M]^+$, base peak), 153, 147, 128, 120, 114, 92, 90, 64, 63.

2. Verification of Previous Attempts at Nitroacetylene Synthesis from 1-Bromo-1-nitroolefins.

2-Phenyl-1, 2-dibromo-1-nitroethane^[64, 65] (18c).



26.3 g (0.164 mole) of bromine in 50 ml of chloroform was added to a solution of 24.5 g (0.164 mole) β -nitrostyrene (15c) in 50 ml of chloroform and refluxed for two hours. Evaporation of the solvent and recrystallization from benzene-petroleum ether (b.p. 40-60°) gave 46.9 g (92%) 2-phenyl-1,2-dibromo-1-nitroethane (18c), m.p. 86° in agreement with the literature^[64, 65].

Analysis calc. for $\text{C}_8\text{H}_7\text{Br}_2\text{NO}_2$:

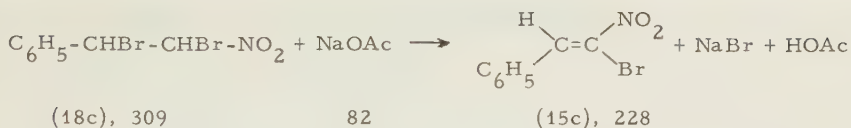
C 31.08, H 2.27, Br 51.75, N 4.56, O 10.35

found C 31.40, H 2.42, Br 51.05, N 4.61, O 10.04

IR (KBr disc): 3050 cm^{-1} (C-H val, arom.), 1578 (C-C arom.), 1565 (NO_2 asym. stretch.), 1500, 1460 (arom.), 1360 (NO_2 sym. stretch.); 775, 697 (C-H out-of-plane def., 5 adjacent free H).

NMR (CDCl_3): δ = 5.48 ppm (1H, d, $\text{C}_6\text{H}_5\text{-CH}$), 6.34 (1H, d, CH-NO_2), 7.41 (5 p, s, C_6H_5); J = 10.2 cps (aliphatic H).

2-Phenyl-1-bromo-1-nitroethylene^[64, 65] (15c).



4.83 g (0.059 mole) of sodium acetate were dissolved in a little water and diluted with 150 ml ethanol. This solution was rapidly added to 18.2 g (0.059 mole) of 2-phenyl-1,2-dibromo-1-nitroethane (18c) in 200 ml of ethanol. The mixture turned yellow immediately. The solvent was removed in vacuo, the residue taken up with ether. After filtering through Na_2SO_4 and removal of ether one recrystallization from ethanol gave 12.45 g (92.5%) of 2-phenyl-1-bromo-1-nitroethylene (15c) as yellow needles, m.p. 64° (Thiele and Haeckel^[65] reported 67°).

Analysis calc. for $\text{C}_8\text{H}_6\text{BrNO}_2$:

C 42.14, H 2.65, Br 35.04, N 6.14, O 14.03

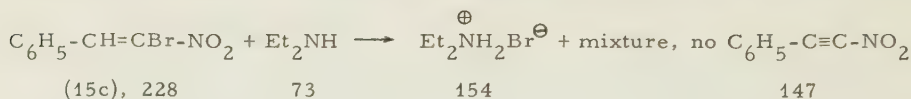
found C 41.95, H 2.72, Br 34.48, N 6.42, O 14.08

IR (KBr disc) : 3030 cm^{-1} (=C-H stretch.), 1615 s (C=C stretch.), 1575 (aromat.), 1540 (NO_2 asym. stretch.), 1490 and 1450 (aromat.), 1312 (NO_2 sym. stretch.), 860 (=C-H out-of-plane def.), 763 , 754 and 689 (C-H out-of-plane def. from 5 adjacent H).

NMR (CDCl_3) : $\delta = 7.3\text{-}8.0$ ppm (5H, m, C_6H_5), 8.62 (1H, s, H-C=).

UV (in n-hexane) : λ_{max} 229 nm ($\log \epsilon$ 3.88), 313.5 nm (4.11).

Reaction of 2-phenyl-1-bromo-1-nitroethylene (15c) with diethylamine^[2b]



To a solution of 5.75 g (25 mmoles) of phenyl-1-bromo-1-nitroethylene (15c) in 60 ml of ether was added 1.84 g (25.2 mmoles) of diethylamine and this mixture heated under reflux. Ten minutes later a white salt precipitated and the colour of the solution slowly turned to red-brown. After 8 hours the mixture was filtered from ca. 2g (51%) of diethylammonium bromide and the ether was distilled off. The residual dark red-brown oil was submitted to TLC (silicagel, 2-propanol-cyclohexane 1:9, detection by UV 254 nm): it showed the presence of starting product along with at least three other compounds.

Analysis calc. for $\text{C}_8\text{H}_5\text{NO}_2$:

C 65.30, H 3.43, N 9.52, O 21.75, Br -

found C 49.87, H 4.57, N 8.89, O 13.94, Br 18.82

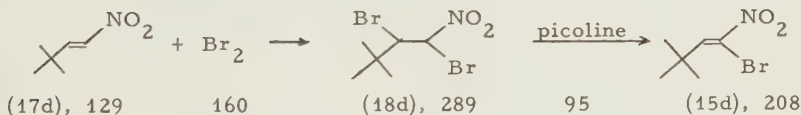
Loevenich and Gerber^[2b] reported 9.62% N.

The reaction was followed by IR and showed no $\text{C}\equiv\text{C}$ infrared absorption at any stage ; GLC of the ethereal solution after 8 hours of reflux showed starting product (207°) and benzaldehyde (115°).

3. Synthesis of 1-Bromo-1-Nitroolefins.

For the preparation of 2-phenyl-1-bromo-1-nitroethylene (15c), see p. 174 f.

1-Bromo-3, 3-dimethyl-1-nitrobutene.



This bromonitroolefin, (15d), was obtained according to the prescription of Heywood et al. [32].

α) 1,2-Dibromo-3,3-dimethyl-1-nitrobutane (18d).

2.25 g (17.5 mmoles) of tert-butylnitroethylene^[32,217] (17d), 2.8 g (17.5 mmoles) of bromine and 0.125 ml conc. HCl in 50 ml CHCl₃ were stirred magnetically for 20 hours at room temperature. The yellow mixture was washed with water, dried over Na₂SO₄ and evaporated to give 4.37 g (87%) of yellow, liquid 1,2-dibromo-3,3-dimethyl-1-nitroethane (18d).

Analysis calc. for C₆H₁₁Br₂NO₂ :

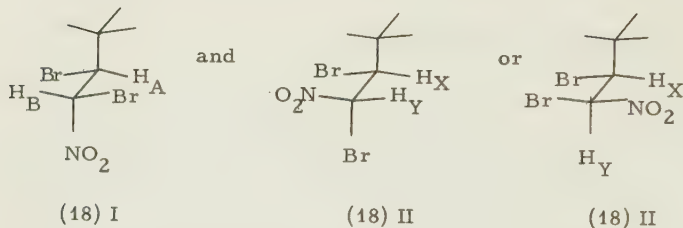
C 25.04, H 3.85, Br 55.15, N 4.86, O 11.13

found C 25.04, H 3.84, Br 55.20, N 5.19, O 11.27

m.w. calc. 289.0, found 278 (THF).

[217] I am obliged to Mr. M. Hartemink, ERA, for supplying this nitroolefin.

NMR (CCl_4) : at room temperature the compound is a 2:1 mixture of two rotamers I and II, probably



(18) I, ca. 65% : δ = 1.28 ppm (9H, s, $\text{C}(\text{CH}_3)_3$), 4.43 (1H, d, H_A), 6.08 (1H, d, H_B), J_{AB} = 7.5 cps.

(18) II, ca. 35% : δ = 1.22 ppm (9H, s, $\text{C}(\text{CH}_3)_3$), 4.71 (1H, d, H_X), 6.30 (1H, d, H_Y), J_{XY} = 2.5 cps.

IR (film) : 1570 (NO_2 asym. stretch.), 1479, 1466, 1401 and 1370 (tert-butyl C-H and skeletal def.), 1350 (NO_2 sym. stretch.).

6) 1-Bromo-3,3-dimethyl-1-nitrobutene^[32] (15d).

Without isolation of the dibromo adduct the solution obtained from 4.5 g (34.9 mmols) of 3,3-dimethyl-1-nitrobutene (17d) and 5.6 g (35.0 mm) bromine, as described above, was diluted with 30 ml of benzene and dried with Na_2SO_4 . After addition of 3.25 g (34.2 mmols) of α -picoline in 5 ml benzene the mixture was stirred for 2 days, extracted three times with water and dried over Na_2SO_4 . Removal of the solvent and bulb tube distillation at 55-60°/0.15 mm gave 6.6 g (91%) of yellow liquid 1-bromo-3,3-dimethyl-1-nitrobutene (15d).

Analysis calc. for $C_6H_{10}NO_2Br$:

C 34.63, H 4.84, Br 38.40, N 6.73, O 15.39

found C 35.47, H 4.94, Br 36.88, N 6.89, O 15.65

m.w. calc. 208.0, found 219 (benzene).

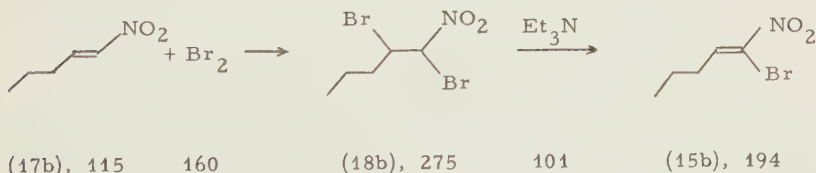
NMR : in CCl_4 : δ = 1.32 ppm (9H, s ; $C(CH_3)_3$), 7.75 (1H, s ; $H-C=$)

in C_6D_6 : 0.84 and 7.49 ppm.

IR (film) : sh 3020 cm^{-1} (=C-H stretch.), 1615 (C=C stretch.), 1547 (NO_2 asym. stretch.) ; 1478, 1465, 1399 and 1370 (t-butyl C-H def. and skeletal vibr.), 1323 (NO_2 sym. stretch.), 1258 and 1204 (t-butyl skel. vibr.), 800 (=C-H out-of-plane def.), 730, 724 (C-N vibr. ?).

UV (n-hexane) : λ_{max} 213 nm (3.60), 263 (3.59).

1-Bromo-1-nitro-pentene (15d).



For this preparation the procedure of Heywood, Durden and O'Dell^[32] was adopted. Loevenich, Koch and Pucknat had obtained this bromo-nitroolefin from 1-nitro-2-pentanol via bromination, acetylation and subsequent elimination of acetic acid^[2a].

α) 1,2-Dibromo-1-nitro-pentane (18b).

3.2 g (0.02 mole) of bromine in 20 ml CHCl_3 was added to 2.30 g (0.02 mole) of 1-nitropentene^[217] in 100 ml of CHCl_3 . After one hour the addition was complete and the solvent removed. 5.18 g (94%) of a yellow liquid were obtained, which darkened on standing.

Analysis calc. for $\text{C}_5\text{H}_9\text{Br}_2\text{NO}_2$:

C 21.80, H 3.30, Br 58.0, N 5.08, O 11.63

found C 23.32, H 3.61, Br 58.24, N 4.83, O 11.42

NMR^[218] (CCl_4) : δ = 0.7-1.2 ppm (3H, distorted triplet, CH_3),
1.2-2.4 (4H, m, CH_2 groups), 4.3-4.7 (1H, split
triplet, $-\text{CHBr}-$), 5.97 (1H, d, $-\text{CHBrNO}_2$; J = 10 cps).

IR (film) : sh 3020 cm^{-1} (C-H stretch.), 1570 and 1352 (NO_2
asym. and sym. stretch.).

β) 1-Bromo-1-nitro-pentene (15b).

To 2.78 g (10.1 mmoles) of 1,2-dibromo-1-nitropentene (18b) in 30 ml of ether 1.01 g (10.0 mmoles) of triethylamine in 10 ml of ether was added. After a few minutes the precipitated ammonium salt was filtered off and the solvent removed. The residue distilled in bulb tubes as a yellow liquid with b.p. $94^\circ/15\text{ mm}$. The yield was 78% (1.53 g) of 1-bromo-1-nitropentene (15b).

Analysis calc. for $\text{C}_5\text{H}_8\text{BrNO}_2$:

C 30.95, H 4.15, Br 41.20, N 7.21, O 16.50

found C 31.91, H 4.35, Br 41.43, N 6.73, O 15.84

m.w. calc. 194.0, found 197 (THF).

NMR (CCl_4) : 0.8-1.2 ppm (3H, t, CH_3), 1.25-1.85 (2H, m, $-\text{CH}_2-$),
2.1-2.6 (2H, q, allylic CH_2), 7.60 (1H, t, olefinic H) ;
coupling constant $J_{=\text{CH}-\text{CH}_2}$ 7.4 cps.

IR (film) : 3030 cm^{-1} ($=\text{C}-\text{H}$ stretch.), 1620 ($\text{C}=\text{C}$ stretch.),
1543, 1322 (NO_2 asym. and sym. stretch.), 773,
758 ($=\text{C}-\text{H}$ out-of-plane def. ?), 720 ($\text{C}-\text{N}$ vibr. ?).

UV (n-hexane) : λ_{max} 215 nm ($\log \epsilon$ 3.57), 263 (3.56).

[218] Varian T-60 spectrometer.

4. Attempted HBr Eliminations from 1-Bromo-1-Nitroolefins.

Compare the control of Loevenich's work, p. 174 f.

From 2-phenyl-1 - bromo-1-nitroethylene (15c).

α) With triethylamine.

7.725 g (25 mmoles) of the dibromo compound (18c) in 100 ml of ether were mixed with 5.00 g (50 mmoles) of triethylamine. The precipitated ammonium salt was filtered. The solution was refluxed 20 hrs. and left for three days at room temperature. The solution contained only undecomposed 2-phenyl-1-bromo-1-nitroethylene (15c) according to its IR spectrum.

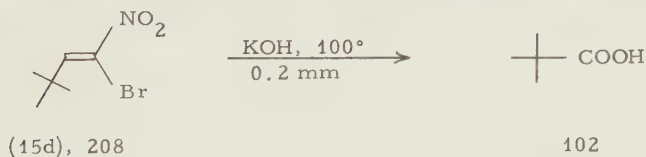
β) With KOH at 130°.

2.28 g (10 mmoles) of the bromo compound (15c) in benzene were added dropwise to a glass tube (80 cm length, 5 cm diameter) packed with anhydrous KOH and heated to 130° [33, 85, 86]. The whole system was attached to an oil pump (0.1 mm), but no distillable product could be trapped. The contents of the tube were extracted with ether. After removal of the solvent the IR spectrum of the residue (mg quantities) showed a carbonyl band at 1705 cm^{-1} , but no longer nitro groups indicating complete decomposition of the starting product.

γ) With sodium acetate in DMF.

2.5 g (33 mmoles) of sodium acetate were given to a solution of 2.0 g (8.8 mmoles) of the phenyl-bromonitroethylene (15c) in 10 ml DMF. The mixture turned immediately dark brown but an IR spectrum showed no absorption in the triple bond region.

From 1-bromo-3,3-dimethyl-1-nitrobutene (15d) with KOH at 100°.



1.1 g (5.3 mmoles) of the bromo-nitroolefin (15d) were distilled at 0.2 mm through a Liebig condenser packed with 70 g KOH and heated to 100° (cf. syntheses of nitroacetylenes p.197 and ref. [1]). Whereas only minor quantities of volatile, non-identified products could be trapped, the potassium hydroxide pellets were covered by a pale-green layer. The KOH was dissolved in water to give a yellow solution which turned colourless when acidified with dil. H_2SO_4 . Extraction with ether, drying over Na_2SO_4 , evaporation and distillation at $\approx 100^\circ/20 \text{ mm}$ gave 363 mg of a semi-liquid product. Analyses and spectra showed it to be pivalic acid (lit. [216] b.p. $70^\circ/14 \text{ mm}$) yield 67%.

5. Synthesis of 2-Halo-1-nitroolefins by Additions of NO_2X to Acetylenes.

a) Addition of nitrylchloride to terminal acetylenes.

Addition of NO_2Cl to phenylacetylene.

According to the procedure reported by Iwai, Tomita, and Ide^[105] trans^[*]-2-phenyl-2-chloro-1-nitroethylene (24a) was obtained in yellow crystals, m. p. 51-52° (lit. 55-56°), yield 35%.

NMR: in CDCl_3 δ =7.42 ppm (s, 5 aromatic and 1 olefinic H coincide) ;
in C_6D_6 6.77 ppm (1H, s, olefinic H), 6.97 (5H, s, aromat.).

IR (film): 1623 cm^{-1} (C=C stretch.), 1535 (NO_2 asym. stretch.), 1450 (aromat.), 1348 (NO_2 sym. stretch.) ; 775, 752, 718 and 693 (=C-H and C-H (5 adj. H) out-of-plane def.), compare lit.^[105].

UV (n-hexane): λ_{max} 223.5 nm (log ϵ 3.98), sh 238.5 (3.94), 277 (3.64), cf. lit.^[105].

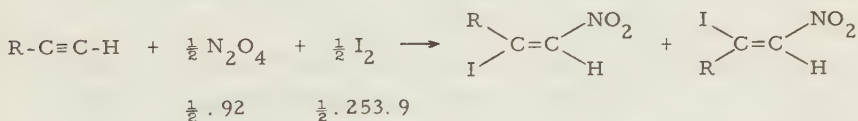
Addition of NO_2Cl to tert-butylacetylene (3,3-dimethyl-1-butyne) in ether.

Nitrylchloride was prepared from chlorosulfonic and nitric acid^[95b,219] and redistilled before use. Ivitzky's procedure^[220a], improved by Hatch et al.^[220b], was applied to synthesize t-butylacetylene.

A solution of 22.7 g (0.28 mole) of nitryl chloride in 50 ml of anhydrous ether (Mallinckrodt p. a.) was added slowly to 15 g (0.183 mole) of tert-butylacetylene in 25 ml of ether. The mixture was stirred at 0° over night.

Besides more than 50% unreacted starting product GLC showed at least 11 compounds. The peak that might have corresponded to the desired compound (35b), 2-chloro-3,3-dimethyl-1-nitrobutene (see p. 209), indicated a yield of only a few percent of this compound.

b) Addition of NO₂-iodine to terminal acetylenes.



Addition of N₂O₄/I₂ to phenylacetylene.

The reaction was carried out as described in the literature^[97]. Only one of the two isomers, (25b), was isolated; yellow needles, m. p. 49-50° in accord with^[97] (25b) is the trans^[*] isomer.

NMR (CCl₄): δ = 7.30 ppm (5H, s, aromat.), 7.62 (1H, s, olefin.).

IR (film): 1615 cm⁻¹ (C=C stretch.), 1597 (aromat.), 1528 (NO₂ asym. stretch.), 1450 (aromat.), 1338 (NO₂ sym. stretch.), 920; 772, 748, 692, 665 (=C-H and CH out-of-plane def.).

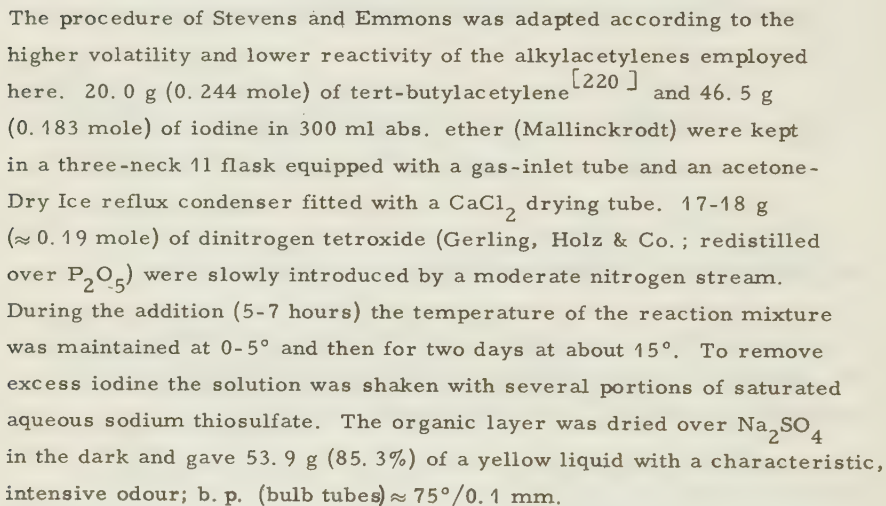
UV (n-hexane): λ_{max} 239.5nm (log ε 4.01), sh 280 (3.80), cp.^[97,110].

[219] K. Dachlauer, D.R. P. 509405 ; C. 1930 II, 3822.

[220] a) P. Ivitzky, Bull. Soc. chim. France 35, 357 (1924);

b) F. Hatch, H.D. Weiss, and T.P. Li, J. org. Chem. 26, 61 (1961).

[*] cis, trans: with respect to the sequence of atomic weights of the substituent atoms.



GLC showed two peaks at 154 and 171° under standard conditions, the more volatile compound (26a) in 16-20% ratio. The less volatile isomer, (26b), 43.4 g, was obtained in 95-97% purity (GLC) by reprecipitating several times from n-pentane at -60 to -80°. The two isomers could be separated by LSC on silicagel, elution with CCl₄; purities were 90-92 and 99-100% (GLC).

Analysis calc. for $C_6H_{10}INO_2$:

C 29.38	H 4.11	I 47.99	N 5.71	O 12.81
found for the crude product (isomer ratio $\approx$ 18:82)				
C 29.00	H 4.32	I 48.71	N 5.19	O 13.19

found for the trans isomer [*] (26a), GLC 154°:

C 29.55 H 4.20 I 48.81 N 5.46 O 12.70

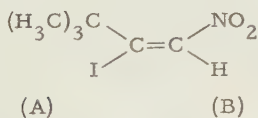
found for the cis isomer (26b), GLC 171°:

C 28.85 H 4.11 I 49.70 N 5.86 O 12.81

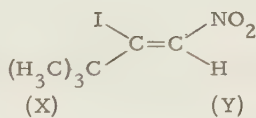
m. w. calc. 255.1, found

crude product 260, trans (26a) 267, cis (26b) 267 (all in benzene).

NMR: a mixture of $\approx 67\%$ of the trans and $\approx 33\%$ of the cis isomer showed the following peaks:



(26a), trans



(26b), cis

in CCl ₄ :	(26a) (A) 1.32	(B) 7.24
	(26b) (X) 1.32	(Y) 7.26

in CCl ₄ with	(26a) (A) 1.28	(B) 7.12
$\approx 15\%$ C ₆ D ₆ :	(26b) (X) 1.24	(Y) 7.15

mixture 5:95	(26a) (A) 0.98	(B) -
in C ₆ D ₆ :	(26b) (X) 0.75	(Y) 6.78 ppm

IR (films)^[221]: trans isomer (26a) 3090 cm⁻¹ (=C-H stretch.); 2976, 2936, 2912, 2875 (t-butyl C-H stretch.); 1645 (C=C stretch.), 1536 (NO₂ asym. stretch.); 1484, 1466, 1401 (t-butyl C-CH₃ and C-H def.); 1369 (NO₂ sym. stretch.), 1282 and 1206 (t-butyl skel. vibrations); 1039, 970, 935, 800 (=C-H out-of-plane def.), 727 (C-N vibr.), 665, 595.

cis isomer (26b) 3095 cm^{-1} ($=\text{C-H}$ stretch.);
 $2977, 2937, 2911, 2875\text{-}70$ (t-butyl C-H stretch.),
 1596 ($\text{C}=\text{C}$ stretch.), 1530 (NO_2 asym. NO_2 stretch.);
 $1480, 1460, 1397, 1368$ (t-butyl C-CH_3 and C-H
 def.), 1340 (NO_2 sym. stretch.); $1276, 1230$ (t-butyl
 skel. vibr.); $1038, 976, 931, 806$ ($=\text{C-H}$ def.), 722
 (C-N vibr.), $560, 516$.

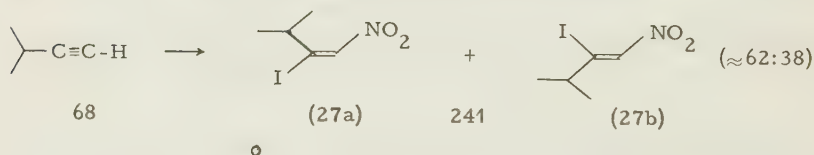
UV: trans (26a), cis tert-butyl and nitro groups !

in n-hexane λ_{max} 211.5 ($\log \epsilon$ 3.85), sh 250 (3.22), sh 335 (2.6)
 in CH_3OH sh 205 (3.89), 216 (3.93), sh 260 (2.90), sh 290 (2.85).

cis (26b)

in n-hexane λ_{max} 208 ($\log \epsilon$ 3.79), sh 240 (3.33), 279 (3.46).

Addition of NO_2 -iodine to iso-propylacetylene (3-methyl-1-butyne).



From 19.8 g (0.291 mole) of i-propylacetylene (Farchan Res. Lab.)
 and 42.6 g (0.168 mole) of iodine in 500 ml of abs. ether with 19.1 g
 (0.208 mole) of N_2O_4 , 60.6 g (86%) of the addition products (27) were
 isolated. GLC analysis showed two peaks at 146 and 161° resp., ratio
 $\approx 62:38$.

[221] Beckmann IR-12 spectrometer; I am grateful to Dr. A. Haag,
 Erlangen, for recording these spectra.

On standing at 0° most of the more volatile isomer (27a) (iodine and NO₂ trans) crystallized. Recrystallization from petroleum ether (b. p. 40-60°) gave yellow needles of (27a), m. p. 40-41° (Tottoli).

LSC of the mother liquor (silicagel; CCl₄) afforded the other isomer (27b), cis-2-iodo-3-methyl-1-nitro-1-butene, a yellow liquid, in pure state. B. p. of the mixture (bulb tubes) ≈ 60°/0.1 mm.

Analysis calc. for C₅H₈INO₂

C 24.92	H 3.35	I 52.65	N 5.81	O 13.28
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found for the trans isomer (27a), GLC 146°

C 24.91	H 3.14	I 53.00	N 5.73	O 13.16
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found for the cis isomer (27b), GLC 161°

C 25.03	H 3.30	I 51.64	N 6.02	O 13.75
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m. w. calc. 241.0; found trans 263, cis 247 (benzene).

NMR (CCl₄):

trans (27a): δ = 1.09 ppm (6H, d, CH₃), 3.39 (1H, "septet", allylic H), 7.52 (1H, "s", olefinic H); J_{CH₃-CH} 6.5 cps.

The allylic coupling constant was too small to be determined exactly.

cis (27b): δ = 1.19 ppm (6H, d, CH₃), 2.55 (1H, "septet", allylic H), 7.43 (1H, "s", olefinic H); J_{CH₃-CH} 6.5 cps, allylic coupling too small for exact evaluation.

IR (films): trans (27a) 3100 cm^{-1} (=C-H stretch.), 1600 (C=C stretch.), 1529 (NO_2 asym. stretch.); 1462, 1387, 1366 (i-propyl C- CH_3 and C-H def.), 1336 (NO_2 sym. stretch.), 1295, 1170 and 1116 (i-propyl skel. vibr. ?), 972, 912, 825 (=C-H out-of-plane def.), 750, 648.

cis (27b) 3080 cm^{-1} (=C-H stretch.), 1603 (C=C stretch.), 1524 (NO_2 asym. stretch.); 1466, 1388 and sh 1366 (i-propyl C- CH_3 and C-H def.), 1340 (NO_2 sym. stretch.), 1264, 1180 and 1110 (i-propyl skel. vibr. ?), 997, 852, 822 (=C-H out-of-plane def.), 746, 735.

UV: trans (27a), cis i-propyl and nitro group.

in n-hexane λ_{max} 212 nm (log ϵ 3.53), sh 243 (3.53),

274 (3.64), sh 291.5 (3.60), sh 301.5 (3.50);

in CH_3OH sh 215 (3.57), sh 275 (3.53), max 295 (3.55).

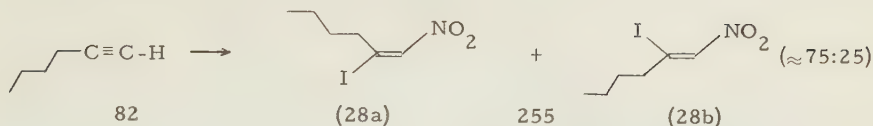
cis (27b) in n-hexane λ_{max} 210 nm (3.78), sh 250 (3.51),

279 (3.63), sh 303 (3.41);

in CH_3OH sh 212 (3.80), 292 (3.59).

Attempts to isomerize the solid trans isomer (27a) (iodine and NO_2 trans) to an equilibrium mixture failed: neither iodine in CCl_4 solution nor N_2O_4 in ether produced significant amounts (< 3%) of the cis compound (27b) after several days.

Addition of NO₂-iodine to 1-hexyne.



13.2 g (0.188 mole) of 1-hexyne (Farchan Res. Lab.) and 35.6 g (0.141 mole) of iodine in 300 ml of dry ether (Mallinckrodt) with 13.0 g (0.141 mole) of N₂O₄ gave 36.8 g (90%) of a yellow liquid that consisted of two isomers in 75:25 ratio (GLC peaks at 171 and 182°). Separation of these isomers by LSC gave 4.32 g of (28a), the trans compound (purity ≈ 98%) and 2.06 g of (28b), the more polar cis compound (purity ≈ 95%) starting from 8.1 g of the crude mixture. B. p. of the mixture ≈ 70°/0.04 mm.

Analysis calc. for C₆H₁₀INO₂

C 29.38 H 4.11 I 47.99 N 5.71 O 12.81

found for the trans isomer (28a), GLC 171°

C 28.62 H 4.06 I 49.48 N 5.44 O 12.51

found for the cis isomer (28b), GLC 182°

C 29.51 H 4.21 I 47.51 N 5.62 O 12.89

m. w. calc. 255.1, found trans (28a) 259, cis (28b) 260 (benzene).

NMR (CCl₄):

trans (28a): δ = 0.8-1.2 ppm (3H, m, CH₃), 1.2-1.9 (4H, m, -(CH₂)₂-), 3.16 (2H, "t", allylic CH₂), 7.52 (1H, t, olefinic H); J_{CH₂-CH} 0.75 cps.

cis (28b): 0.7-1.15 ppm (3H, m, CH₃), 1.15-1.9 (4H, m, -(CH₂)₂-), 2.73 (2H, "t", allylic CH₂), 7.35 (1H, t, olefinic H);
J_{CH₂-CH} 1.1 Hz.

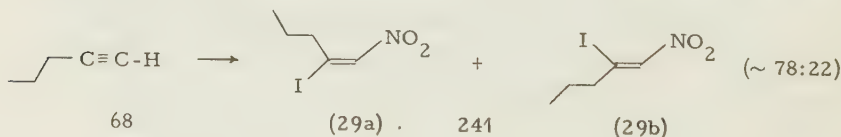
IR (films): trans (28a) 3110 cm⁻¹ (=C-H stretch.), 1610 (C=C stretch.), 1530 (NO₂ asym. stretch.), 1468 and 1435 (C-CH₃ and CH₂ C-H def.), 1336 (NO₂ sym. stretch.), 828 (=C-H out-of-plane def.), 730 (C-N vibr.).

cis (28b) 3080 (=C-H stretch.), 1605 (C=C stretch.), 1524 (NO₂ asym. stretch.), 1466, 1339 (NO₂ sym. stretch.), 1272, 825 (=C-H def.), 732 (C-N vibr.).

UV: trans (28a) in n-hexane λ_{max} sh 213 nm (log ε 3.69), 245.5 (3.63), 275 (3.76);
in CH₃OH 216.5 (3.70), sh 275 (3.68), 292 (3.70).

cis (28b) in n-hexane 212 (3.76), sh 243 (3.52), 279 (3.64), sh 303 (3.40);
in CH₃OH 214 (3.79), 291.5 (3.61).

Addition of NO₂-iodine to 1-pentyne.



17.5 g (0.258 mole) of 1-pentyne (Farchan Res. Lab.) and 45.4 g (0.179 mole) iodine in 300 ml ether along with 17.5 g N_2O_4 (0.18 mole) yielded 35.3 g (57%) of the yellow adducts (29), ratio $\approx$ 78:22 (GLC peaks at 156 and 170°).

LSC of 5.0 g of the isomeric mixture gave 2.76 g of (29a), the trans, (GLC purity 98%) and 0.84 g of (29b), the cis compound (95% purity).

Analysis calc. for $C_5H_8INO_2$

C 24.92 H 3.35 I 52.65 N 5.81 O 13.28

found for the trans isomer (29a), GLC 156°

C 24.88 H 3.35 I 55.57 N 6.01 O 12.91

found for the cis isomer (29b), GLC 170°

C 24.60 H 3.30 I 53.20 N 5.77 O 13.47

m. w. calc. 241.0, found trans (29a) 249, cis (29b) 249 (benzene).

NMR (CCl_4)

trans (29a): δ = 1.02 ppm (3H, distorted triplet, CH_3),

1.35-2.1 (2H, m, $-CH_2-$), 2.97-3.3 (2H, "t", allylic CH_2), 7.56 (1H, "s", olefinic H);

J_{CH_2-CH} 0.8 cps.

cis (29b): 0.99 (2H, "t", CH_3), 1.4-1.95 (2H, m, $-CH_2-$),

2.55-2.9 (2H, "t", allylic CH_2), 7.37 (1H, t,

olefinic H); J_{CH_2-CH} 1.0 cps.

IR (films):

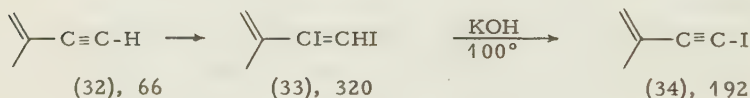
trans (29a) $3110-05\text{ cm}^{-1}$ (=C-H stretch.), 1610 (C=C stretch.), 1530 (asym. NO_2 stretch.), 1460, 1432, 1382 (C- CH_3 , CH_2 def.), 1335 (sym. NO_2 stretch.), 1118, 1088, 985, 850, 825 (=C-H out-of-plane def.), 743 (C-N vibr. ?).

cis (29b) 3080-70 (=C-H stretch.), 1605 (C=C stretch.), 1525 (NO₂ asym. stretch.), 1465, 1385 (CH₃, CH₂ C-H def.), 1340 (NO₂ sym. stretch.), 1283, 969, 820 (=C-H out-of-plane def.), 739 (C-N vibr.).

UV: trans (29a) in n-hexane $\lambda_{\max}$ sh 212 nm (log ϵ 3.70), 243 (3.63), 275 (3.76);
in CH₃OH sh 222 (3.69), 292 (3.74).

cis (29b) in n-hexane 210 (3.72), sh 243 (3.47), 279 (3.60),
sh 288 (3.58), sh 303 (3.36);
in CH₃OH 213 (3.75), 292 (3.61).

Addition of NO₂-iodine to isopropenylacetylene (3-methyl-3-buten-1-yne).



α) 1,2-Diiodo-3-methyl-1,3-butadiene (33)

To a solution of 33.0 g (0.50 mole) of isopropenylacetylene (Farchan Res. Lab.) and 70 g (0.276 mole) of iodine in 1.3 l of abs. ether at 0-5°, 25.3 g (0.275 mole) of N₂O₄ was bubbled in as usual. After three days 7.0 g of an ochre precipitate was filtered off from the mixture. This powder (dec. > 280°) showed nitro groups in the IR spectrum, but because of its insolubility even in solvents as DMSO no further spectra could be obtained. Elemental analysis proved addition of 1.0 NO₂ and 0.6 iodine per two molecules isopropenylacetylene and thus indicated more or less a polymeric compound.

The filtrate was washed with thiosulfate solution to remove iodine and after drying and evaporation yielded 105 g of a dark-brown oil (IR: nitro group absorptions present).

10 g of this crude product were distilled (bulb tubes) at 60° (0.1 mm) to give 7.17 g (47% yield calc. relative to isopropenylacetylene) of a red-brown liquid that decomposed slowly, even at -80°. GLC under standard conditions showed two peaks at 153 and 163°, ratio 40:60. According to analysis, spectra and subsequent HI elimination to yield isopropenyliodoacetylene (34) this liquid was an isomeric mixture of 1,2-diiodo-3-methyl-4,3-butadienes (33).

Analysis calc. for $C_5H_6I_2$

	C 18.75	H 1.875	I 79.38	O -
found	C 18.30	H 1.81	I 77.49	O 1.75

m. w. calc. 319.9, found 357 (benzene).

NMR (CCl_4): two isomers A, B (~35:65)

A δ = 2.07 ppm (3H, "s", CH_3); 5.24, 5.42 (1H each, two split peaks, methylene protons), 7.52 (1H, s, =CHI).

B δ = 1.92 ppm (3H, t, $J \approx 1$ cps; CH_3), 5.12 (2H, m, = CH_2), 6.87 (1H, s, =CHI).

IR (film): 3060 cm^{-1} (=C-H stretch.), 1810 (overtone of the 904 cm^{-1} = CH_2 out-of-plane def.), 1685 (C=C stretch. of I-C=C-I), 1612 (C=C stretch. of the C= CH_2 group), 1560, 1527, 1450 (CH_3 asym. def.), 1440 (= CH_2 in-plane def.), 1370 (CH_3 sym. def.), 1269, 1184, 975 (-CH=CH- def.), 904 (= CH_2 out-of-plane def.), 773, 721.

UV (in 2-propanol): $\lambda_{\max}$ sh 205 nm (log ϵ 3.87), sh 230 (3.68),
291 (4.10), 360 (3.86).

β) 1-Iodo-3-methyl-3-buten-1-yne (34).

1.5 g (4.7 mmoles) of the diiodo compound mixture (33) was distilled through a KOH packed tube (cp. p. 197) at 100°/0.4 mm. The acetone-Dry Ice cooled receiver contained 0.72 g (80%) of the iodoacetylene (34), a pale-yellow volatile liquid with leek-like odour, that decomposed on standing at room temperature.

Analysis calc. for C_5H_5I

	C 31.28	H 2.63	I 66.10
found [222]			
	C 29.84	H 3.63	I 63.41

NMR (CCl_4): δ = 1.86 ppm (3H, "s", CH_3), 6.18 and 6.27 (2H, two "quartets", methylene H); $J_{CH_3-H_{trans}} \approx 0.8$ cps,
 $J_{CH_3-H_{cis}} \approx 1.8$ cps.

IR (CCl_4): 3095 cm^{-1} (=C-H stretch.), 2955 and 2920 (CH_3 C-H stretch.), 2170 ($C\equiv C$ stretch.), 1810 (overtone of the $=CH_2$ out-of-plane def. vibration at 900 cm^{-1}), 1610 ($C=C$ stretch.), 1450 (CH_3 asym. def.), 1433 ($=CH_2$ in-plane def.), 1374 (CH_3 sym. def.), 1278, 1014, 900 ($=CH_2$ out-of-plane def.), 838.

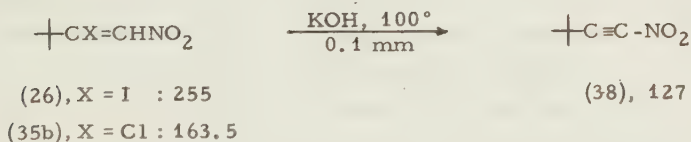
UV (n-hexane): $\lambda_{\max}$ sh 214 nm (log ϵ 3.79), sh 224 (4.04), 231.5 (4.14), sh 240 (3.97).

[222] Though GLC and NMR showed a pure compound, incomplete combustion and decomposition led to differing values for C, H, I.

6. Synthesis of Nitroacetylenes by Elimination of HX from 2-Halo-1-nitroolefins

Eliminations from 2-phenyl-2-chloro-1-nitroethylene (24a), the corresponding 2-iodo compound (25a) and the isomeric t-butyl 2-iodo-1-nitroethylenes (26) were tried with a number of reagents, such as tertiary amines, sodium acetate, silver oxide, potassium t-butyrate under varying conditions. IR spectra showed many different decomposition products, because HX eliminations took place especially with $\text{KOC}(\text{CH}_3)_3$ and tert. amines. At best in a few runs the $\text{C}\equiv\text{C}$ triple bond absorption reached 95% transmittance (100% $\hat{=}$ no absorption).

Tert. -butylnitroacetylene (38) (3,3-dimethyl-1-nitrobutyne)^[1]



5.0 g (19.6 mmoles) of the 2-iodo-3,3-dimethyl-1-nitro-1-butene mixture (26) were distilled within about 5 hours through a Liebig condenser (length 30 cm, internal diameter 1.5 cm) containing 70 g of potassium hydroxide pellets and heated to 100°, in a way similar to a bulb tube distillation. The distillation started at $\approx 75^\circ/0.1 \text{ mm}$ (air bath). The contents of the receiver which was cooled by acetone-Dry Ice, were dissolved in n-pentane. The solution was dried by filtering through Na_2SO_4 and the solvent was removed in vacuo, leaving 2.42 g (96%) of a pale yellowish green, volatile, strongly lachrymatory liquid having a m. p. $\approx -3^\circ$ and b. p. $\approx 55^\circ/15 \text{ mm}$. GLC showed more than 98% purity, temperature 107° vs. 119° of the corresponding nitroolefin (17d)^[32, 217]. Comparison of the peak areas of these two compounds indicated no decomposition of tert. -butylnitroacetylene (38).

In an analogous preparation from 0.584 g (3.57 mmoles) 2-chloro-3,3-dimethyl-1-nitro-1-butene (35b) at 45-47° air bath temperature - 100° elimination temperature - 0.1 mm 0.312 g (69%) of t-butylnitroacetylene (38) were obtained (one run only).

Analysis calc. for $C_6H_9NO_2$:

C 56.68, H 7.14, N 11.02, O 25.17

found C 57.19, H 7.31, N 11.14, O 25.16

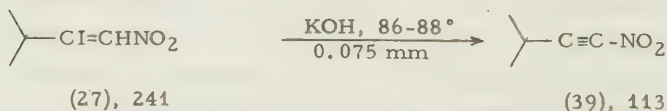
NMR in CCl_4 : $\delta = 1.34$ ppm, s;

in C_6D_6 : 0.75 ppm.

IR (film)^[221] : 2981 cm^{-1} , 2939, 2913, 2876 and 2835 (t-butyl C-H stretch.), 2270 and 2231 ($C\equiv C$ stretch. disubstituted acetylene), 1513-12 (NO_2 asym. stretch.), 1481, 1468, 1388 and 1370 (C-H def.), 1352 (NO_2 sym. stretch.), 1254 and 1205 (t-butyl skel. vibrations), 935, 844, 737 and 730.5 (C-N vibr.), 530.

UV (n-hexane) : λ_{max} 238 nm (log ϵ 3.90).

Iso-propylnitroacetylene (39) (3-methyl-1-nitro-1-butyne).



The reaction was carried out similarly to that described above. The distillation started at 60-62°/0.075 mm and the elimination tube was heated to 86-88°. During the distillation (4 hours) the KOH pellets became covered by a red-brown layer; when this colour became too dark decom-

position of the iso-propylnitroacetylene (39) was predominant because of too high temperature. The contents of the cooled flask were distilled at 0°/0.1 mm from undecomposed starting product (27) into a second bulb tube, cooled at -80°. 2.05 g (8.5 mmoles) of the iodo-nitroolefin (27), thus yielded 0.716 g (74%) of iso-propyl-nitroacetylene (39). Its properties were similar to the t-butyl derivative (38).

This nitroacetylene passed at 104° (GLC) with partial decomposition, purity (NMR) > 98%.

Analysis calc. for C₅H₇NO₂ :

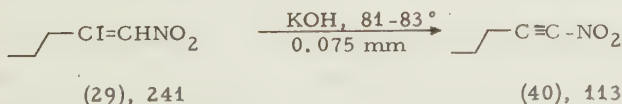
 C 53.09, H 6.24, N 12.38
found^[223] C 49.52, H 6.18, N 10.5 .

NMR (CCl₄) : δ = 1.30 ppm (6H, d, CH₃), 2.8 (1H, septet, propargylic H); J_{CH₃-CH} 6.5 cps.

IR (film) : 2980 cm⁻¹ and sh 2940, sh 2880 (C-H stretch.), 2245 and sh 2210 (C≡C stretch. disubst. acetylene), 1510 (NO₂ asym. stretch.), 1466 and 1388 (C-H def.), 1345 (NO₂ sym. stretch.), 878, 780 (i-propyl skel. vibr.), 730 (C-N vibr.).

UV (cyclohexane) : λ_{max} 239.5 nm (log ε 3.81), sh 290 (2.25).

n-Propylnitroacetylene (40) (1-nitro-1-pentyne)



[223] Incorrect values because complete combustion of capillary contents could not be achieved. Too volatile for combustion from an open boat.

1-Nitro-1-pentyne (40) was prepared by distilling 1.0 g (4.15 mmoles) of the iodo-nitroolefin mixture (29) from an air bath of 50-52° at 0.075 mm. The KOH pellets turned dark-brown. To remove unchanged starting product, the contents of the cooled receiver (-80°) were re-distilled through an ice-cooled bulb tube and condensed at -80°. The yield was 28% (148 mg) of n-propylnitroacetylene (40); purity 90% (NMR) with 10% trans starting compound (29a). This nitroacetylene was both too volatile and unstable to run CHN analysis. On GLC analysis under standard conditions extensive decomposition was observed.

NMR (CCl₄) : δ = 0.85 - 1.25 ppm (3H, m, CH₃), 1.35 - 1.95 (2H, m, CH₂), 2.3 - 2.6 (2H, "t", propargylic CH₂), impurity $\approx$ 10% trans-2-iodo-1-nitro-1-pentene (29a).

IR (film) : 2980 cm⁻¹, 2960 and 2890 (C-H stretch.), 2450 (very weak band, ?), 2260 and sh 2200 (C $\equiv$ C stretch. of disubst. acetylene), 1515 (NO₂ asym. stretch.), 1465, sh 1425, sh 1389 (C-H def.), 1358 (NO₂ sym. stretch.), 835, 826, 770, 730 (C-N vibr., ?);

impurities : weak band at 1735 (C=O stretch., probably from the hydrated product 1-nitro-2-pentanone); 3100 and 1615 (weak bands from the trans starting compound (29a)).

UV (n-hexane) : $\lambda_{\max}$ 235 nm (3.88).

n-Butyl- and phenylnitroacetylene (41) and (42), resp. (1-nitro-1-hexyne and 2-phenyl-1-nitroacetylene)

The nitroacetylenes (41) and (42) could not be isolated in pure state. Eliminations from 2-iodo-1-nitro-1-hexenes (28) and 2-chloro-2-phenyl-1-nitroethylene (24a) gave mixtures that showed C $\equiv$ C absorptions in

the IR at 2265 (n-butyl) and $\approx 2240 \text{ cm}^{-1}$ (phenyl compound). Both triple bond absorptions disappeared after a few hours, indicating the instability of these nitroacetylenes.

7. Thermal Stability of tert-Butylnitroacetylene.

Decomposition at room temperature.

2.46 g (19.4 mmoles) of tert-butylnitroacetylene (38) after 30 days at room temperature still showed a triple bond absorption in the IR spectrum, transmission 60% (originally 20%). From a GLC analysis it was shown that about 15% of the volatile components (more than 20 peaks) was unchanged nitroacetylene. The NMR spectrum of the liquid showed more than 18 peaks in the t-butyl region (1.1-1.6 ppm).

From the mother liquor by filtering and washing with n-pentane 24 mg (1.0%) of colourless crystals were isolated, m.p. under decomposition 167-168°.

Analysis calc. for $C_{12}H_{18}N_4O_8$

C 41.62, H 5.24, N 16.18, O 36.96

found C 41.33, H 5.32, N 16.12, O 36.49

m.w. calc. 346.3, found 332 ($CHCl_3$).

NMR ($CDCl_3$) : one peak at $\delta = 1.41$ ppm.

IR ($CHCl_3$) : 1600 cm^{-1} , 1580 ; 1488, 1472, 1405, 1372 (prob. t-butyl C-H def.), 1362, 1340, 1322, 1300, 1165, 837, 832, 817 ; 751, 732 and 695 (from a KBr disk).

UV (n-hexane) : λ_{max} sh or max 200 (4.33), 283 (2.57).

Tert-butylnitroacetylene (38) in μl quantities passed unchanged at GLC analyses (105-115°), but decomposed considerably on a preparative column. For example, from 0.7 g (38) of about 95% purity, only 60 mg could be recovered by preparative GLC.

In a sample of tert-butylnitroacetylene (38), which was heated on a steam bath for two hours only a trace of the original strong $\text{C}\equiv\text{C}$ absorption could be observed in the IR.

acid. The amide was extracted with ether from the aqueous solution and washed with saturated NaHCO_3 solution. The ether was removed and as the product still showed additional $\text{C}=\text{O}$ bands in the IR spectrum, probably due to an anhydride, the residue was heated with water. Recrystallization from methanol-ether yielded 164 mg (25%) of the dinitro benzamide (44), m.p. $122-123^\circ$.

Analysis calc. for $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_5$

C 52.87, H 5.80, N 14.23, O 27.09

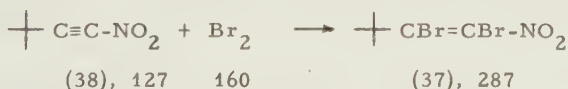
found C 52.95, H 5.94, N 14.04, O 27.18

m.w. calc. 295.3, found 293.5 (THF).

NMR (D_6 -DMSO + 20% $\text{CF}_3\text{-COOD}$) : $\delta = 1.0$ ppm (9H, s, CH_3),
 1.2-1.7 (2H, m, $\text{C-CH}_2\text{-C}$), 3.2-3.6 (2H, m, $\text{C-CH}_2\text{-N}$),
 9.0 (1H, m, aromatic 4-H), 9.2 (2H, m, aromatic
 2,6-H), 15.6 (1H, s, exchanged H in CF_3COOD).

IR (KBr disk) : 3300 cm^{-1} and 3100 (N-H stretch.), 2980 and 2880
 (C-H stretch.), 1645 (amide I), 1580 (aromat.),
 1540 (NO_2 asym. stretch.), 1452 (aromat.), 1365
 (C-H def.), 1345 (NO_2 sym. stretch.), 1333, 1317,
 922 (C-H out-of-plane def. of 1 free H), 729, 722.

b) Addition of bromine: 1, 2-Dibromo-3, 3-dimethyl-1-nitro-1-butene (37).



To 1.272 g (10 mmoles) of tert-butyl nitroacetylene (38) a solution of 2.0 g (12.5 mmoles) of bromine in 10 ml CHCl_3 was added. The mixture warmed up to $\approx 40^\circ$ and stood at room temperature over night. Bulb tube distillation, after removal of the solvent and excess bromine on a rotavapor, gave 2.72 g (95%) of (37), a yellow-golden liquid, b. p. $\approx 80^\circ/0.1$ mm.

Analysis calc. for $\text{C}_6\text{H}_9\text{Br}_2\text{NO}_2$:

C 25.11, H 3.16, Br 55.70, N 4.88, O 11.15

found C 25.54, H 3.17, Br 54.44, N 4.92, O 11.18

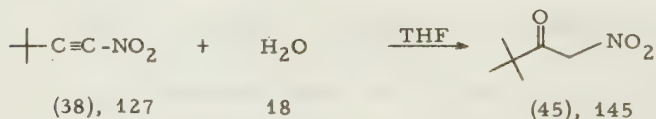
NMR (CCl_4) : one peak at $\delta = 1.5$ ppm.

IR (film) : 2980 and 2880 cm^{-1} (C-H stretch.), 1550 (C=C and NO_2 asym. stretch. coinciding ?), 1480, 1465, 1403 and 1370 (C-H def.), 1348 (sym. NO_2 stretch.), 1222 and 1205 (t-butyl skel. vibr.), 813, 772, 725 (C-N vibr.).

UV (n-hexane) : λ_{max} 212 nm (4.12), 284 (2.53), sh 340 (1.96).

c) Addition of water and alcohols to tert-butyl nitroacetylene

α) Addition of water : 3,3-Dimethyl-1-nitro-2-butanone (45)



A solution of 562 mg (2.26 mmoles) of tert-butyl nitroacetylene (38) and 0.5 g (27.8 mmoles) of water in 5 ml THF was prepared. After 24 hours the solvent was evaporated, ether added and dried over CaCl_2 . Fractional distillation

(bulb tubes) at $\approx 110^\circ/15$ mm yielded 474 mg (74%) of (45), a pale yellow liquid; GLC 136-137°.

This α -nitro ketone did not form a hydrazone under conditions reported for other α -nitro ketones^[139].

Analysis calc. for $C_6H_{11}NO_3$:

C 49.64, H 7.64, N 9.65, O 33.07

found C 49.32, H 7.78, N 9.47, O 32.72

NMR (CCl_4) :

keto-enol equilibrium with 15-17% enol,

keto form $\delta = 1.22$ ppm (9H, s, CH_3), 5.38 (2H, s, CH_2);

enol form $\delta = 1.24$ ppm (9H, s, CH_3), 6.75 (1H, s, $=CH-$),

the enolic proton was not located.

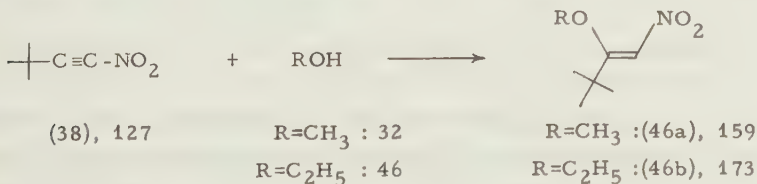
IR (film) :

sh 3020 cm^{-1} , 2980 and sh 2900 (C-H stretch.), 1720-15 (C=O stretch.), 1570 (asym. NO_2 stretch.), 1483, 1402, 1375 (C-H def.), 1385 and 1321 (sym. NO_2 stretch. and C-O vibr.), 1230 and sh 1211 (t-butyl skel. vibr.), 1191, 1065, 1016, 690.

UV in n-hexane : $\lambda_{\max}$ sh 240 (3.03), 298 (3.46);

in methanol : sh 230 (3.28), 325 (283).

β) Addition of alcohols: 3,3-Dimethyl-2-methoxy- and 2-ethoxy-1-nitro-1-butene



200-300 mg of tert-butylnitroacetylene (38) in 5 ml of the absolute alcohol (R as above) stood for 24 hours at room temperature. Excess alcohol was removed to leave the nitro enolethers (46) as yellow easily hydrolysing liquids.

265 mg (2.09 mmoles) of the nitroacetylene (38) yielded 287 mg (86%) of 3,3-dimethyl-2-methoxy-1-nitro-1-butene (46a); b. p. 45-50° (0.1 mm).
GLC analysis : peaks at 136° (2%, ketone ?), 146° (95%, cis, i.e. methoxy and nitro groups cis), and 159° (3%, trans ?).

Analysis calc. for $C_7H_{13}NO_3$:

C 52.81, H 8.23, N 8.80, O 30.15

found C 53.26, H 8.62, N 9.05, O 30.24

m.w. calc. 159.2, found 177 (THF).

NMR (in CCl_4) showed a 85:10:5 mixture (cis, trans, unknown).

cis δ = 1.15 ppm (9H, s, t-Bu), 3.9 (3H, s, OCH_3), 6.6 (1H, s, olefinic H);

trans δ = 1.27 ppm (9H, s, t-Bu), 3.7 (3H, s, OCH_3), 6.55 (1H, s, olefinic H);

unknown impurity : 1.53 ppm (9H, s, t-Bu), 3.4 (3H, s, OCH_3).

IR (film) : 3150 cm^{-1} (=C-H stretch.), 1740 (weak C-O str. of α -nitro ketone impurity), 1618 (C=C stretch.), 1566, 1505 (NO_2 asym. stretch. ?), 1460 (C-H def.), 1356 and 1320 (NO_2 sym. and =C-O- stretch?), 1265, 1243, 1220, 1176, 1145, 1040, 995, 872, 820, 785, 736.

UV (n-hexane) : λ_{max} sh 220 nm (log ϵ 3.55), 268 (3.69), sh 335 (2.8).

In ethanol from 403 mg (3.17 mmoles) of the nitroacetylene (38) 430 mg (78%) of the ethoxy compound (46b) were obtained. GLC analysis : peaks at 144° (4%) and 155° (96%, cis).

Analysis calc. for $C_8H_{15}NO_3$:

C 55.47, H 8.73, N 8.99, O 27.71

found C 55.86, H 8.40, N 9.56, O 28.13

m.w. calc. 173.2, found 188 (THF).

NMR (CCl_4) :

a sample obtained by preparative GLC (purity > 99%) showed about 10% of a second t-butyl group at 1.30 ppm, that corresponded probably to another, possibly the trans isomer.

cis δ = 1.16 ppm (9H, s, t-Bu), 1.35 (3H, t, ethyl CH_3), 4.1 (2H, q, O- CH_2), 6.6 (1H, s, olefinic H); $J_{CH_3-CH_2}$ 7 cps.

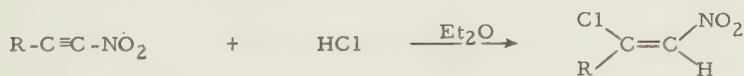
IR (film) :

3150 cm^{-1} (=C-H stretch.), 2980 and 2880 (C-H stretch.); 1740 (weak C=O stretch. from hydrolysed product), 1615 (C=C stretch.), 1532, 1515, 1505 (NO_2 asym. stretch. ?), 1470, 1397 and 1379 (C-H def.), 1355 and 1319 (sym. NO_2 and =C-O- stretch. ?), 1148, 1040, 1013, 850, 767, 732.

UV (n-hexane) :

λ_{max} sh 220 (3.67), 267.5 (3.88), sh 335 (2.87).

d) Addition of hydrogen chloride to tert-butyl- and iso-propylnitroacetylene (38) and (39), resp. : 2-Chloro-1-nitroolefins



R=t-Bu : (38), 127.1

36.5

R=t-Bu : (35b), 163.6

R=i-Pr : (39), 113.1

R=i-Pr : (36b), 149.6

The nitroacetylene in abs. ether was added to a dry solution of hydrogen chloride (5-10 fold excess) in ether. Removal of the solvent and bulb tube distillation gave the 2-chloro-1-nitroolefins, yellow, quite volatile lachrymatory liquids.

α) cis-2-Chloro-3,3-dimethyl-1-nitro-1-butene (35b)

637 mg (5.0 mmoles) of tert-butylnitroacetylene (38) afforded 773 mg (94%) of the cis-2-chloro-1-nitroolefin (35b), b. p. $\approx 40^\circ/0.1$ mm. GLC : two peaks at 127° and 145° , ratio 3 : 97.

Analysis calc. for $C_6H_{10}ClNO_2$:

C 44.05, H 6.16, Cl 21.67, N 8.56, O 19.55

found C 43.60, H 6.15, Cl 21.39, N 8.34, O 19.98

m.w. calc. 163.6, found 178 (THF).

NMR (CCl_4) : $\delta = 1.30$ ppm (9H, s, CH_3), 7.15 (1H, s, olefinic H).

IR (film) : 3120 cm^{-1} (=C-H stretch.), 1615 (C=C stretch.), 1532 (NO_2 asym. stretch.); 1480-60 broad, sh 1402, and sh 1378 (C-H def.), 1348 (NO_2 sym. stretch.), 1282, 1247 and sh 1205 (t-butyl skel. vibr.), 1044, 1005, 813 (=C-H out-of-plane def.), 743 (C-N vibr.), 708.

UV (in n-hexane) : $\lambda_{\max}$ 246 nm (3.80), sh 300 (2.42);
(in methanol) : 255 nm (3.69), sh 330 (2.47).

β) cis-2-Chloro-3-methyl-1-nitro-1-butene (36b)

From ca. 80 mg (≈ 0.7 mmole) iso-propylnitroacetylene ($\approx 90\%$ purity) 51 mg (ca. 50%^[225]) of the cis-2-chloro-1-nitroolefin (36b) were isolated, b. p. $\approx 35^\circ/0.1$ mm. GLC : two peaks at 136° (94%) and 148° (6%, trans-2-iodo-3-methyl-1-nitro-1-butene (27a), starting product for the nitroacetylene preparation).

[225] Relatively low yield because of the volatility of the adduct.

Analysis calc. for $C_5H_8ClNO_2$:

 C 40.14, H 5.39, N 9.37, O 21.39
found [226] C 37.93, H 5.31, N 9.02, O 20.57

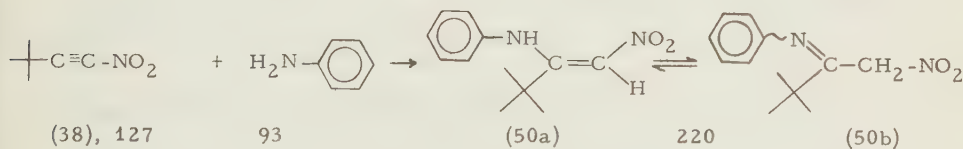
NMR (CCl_4) : δ = 1.25 ppm (6H, d, CH_3), 2.7 (1H, septet, allylic H),
7.25 (1H, s, olefinic H); J_{CH_3-CH} = 6.8 cps, allylic
coupling constant J - 0.6 cps.

IR (film) : 3115 cm^{-1} (=C-H stretch.), 1625 cm^{-1} (C=C stretch.), 1530
(NO_2 asym. stretch); 1470 and 1392 cm^{-1} (C-H def.), 1351
(NO_2 sym. stretch.), 1270 , 1028 , 1005 , 878 , 815 cm^{-1} (=C-H
out-of-plane def.), 750 cm^{-1} (C-N vibr.), $710-5$.

UV (in n-hexane) : λ_{max} 246 nm (log ϵ 3.84), sh 300 (2.64);
(in methanol) : 256 nm (3.76).

e) Addition of primary and secondary amines to tert-butylnitroacetylene (38)

$\alphaAddition of aniline$



To a solution of 476 mg (5.11 mmoles) of aniline in 10 ml of abs. ether was added dropwise 635 mg (5.0 mmoles) of tert-butylnitroacetylene (38) in 25 ml of ether. After that the solvents were distilled off and the residue recrystallized from ether-n-hexane to yield 504 mg (46%) of (50a), yellow crystals, m. p. $108-109^\circ$.

[226] Too low values due to $\approx 10\%$ iodo-nitroolefin.

Analysis calc. for $C_{12}H_{16}N_2O_2$:

C 65.43, H 7.32, N 12.72, O 14.53

found C 65.66, H 7.44, N 12.78, O 14.73

m.w. calc. 220.3, found 244 (benzene).

NMR : in $CDCl_3$ at room temperature the product consisted of a tautomeric enamine - imine mixture with 36-37% imine (50b).

enamine (50a) δ = 1.17 ppm (9H, s, CH_3), 6.97 (1H, s, olefinic H),
12.1 (0.6H, broadened, -NH-);

imine (50b) δ = 1.31 ppm (9H, s, CH_3), 5.1 (2H, s, CH_2).

The phenyl protons were indistinguishable and appeared at 6.75-6.85 and 7.55 - 7.70 ppm, both multiplets.

At -60° in $CDCl_3$ three isomers were present (70 : 26 : 4 ratio) :

enamine (50a) δ = 1.21 ppm, 7.18 (olefinic H);

imine (50b) δ = 1.32 ppm, 5.23; a third isomer exhibited peaks at
1.27 (t-butyl) and 5.8 ppm (CH_2).

In DMSO the ratio enamine (50a)-imine (50b) was $\approx$ 94 : 6 :

enamine (50a) δ = 6.77 ppm (1H, s, olefinic H), 12.6 (0.5H, broadened, -NH-);

imine (50b) δ = 5.42 ppm (2H, s, CH_2). The tert-butyl protons coalesced at 1.27, the phenyl protons appeared at 6.9 - 7.5 ppm.

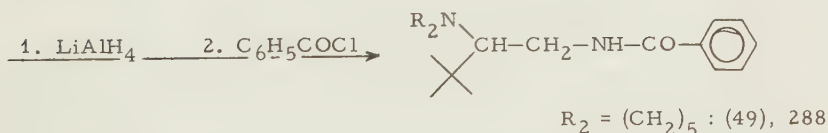
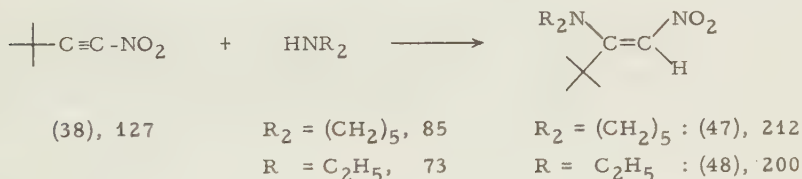
IR (KBr disc) : 3180 cm^{-1} (N-H or =C-H stretch.), 1580 and 1570 ($C=C$ and NO_2 asym. stretch.), 1483 (C-H def.), 1455 (aromat.), 1350 (sym. NO_2 stretch), 1272, 1247, 1181, 1164, 938, 797, 770, 748 and 697 (C-H out-of-plane def. of 5 adjacent H), 667.

UV (in methanol) : $\lambda_{\max}$ 240 nm (3.93), 358 (4.03);

in 0.65% NaOH in methanol 307 (3.70), in methanol with
0.4% HCl 207.5 (3.94), sh 235 (3.22), 290 (2.47).

In chloroform the 358 nm absorption changed its intensity
from $\epsilon = 19200$ ($\lg \epsilon$ 4.29) to 13700 (4.14) within 5 h.

β) Addition of secondary amines, piperidine and diethylamine



Tert-butyl nitroacetylene (38) in ether was added to a solution of the amine at 0°. Removal of the solvent and recrystallization gave the corresponding nitroenamines.

2-Tert-butyl-2-piperidino-1-nitroethylene (47) :

0.825 g (6.5 mmoles) of tert-butyl nitroacetylene in 15 ml ether and 0.70 g (8.2 mmoles) of piperidine in 10 ml ether gave 1.10 g (80%) of (47), yellow crystals, m.p. 60° (from n-hexane).

Analysis calc. from $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_2$:

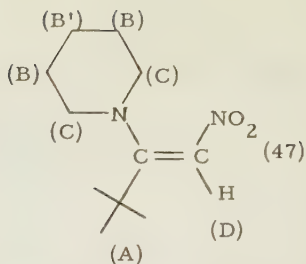
C 62.23, H 9.50, N 13.20

found [227] C 62.10, H 9.50, N 13.37

m.w. calc. 212.3, found 215 (CH_3OH).

[227] I would like to thank Mr. H. Zankl, Erlangen, for performing this analysis.

NMR (CCl_4) : $\delta = 1.31$ ppm (9H, s, A),
 1.7 (6H, broad, B and B'),
 3.1 (4H, broad, C), 6.60
 (1H, s, D).



IR (film) : 3130 cm^{-1} (=C-H stretch.), 1550 (C=C and NO_2 asym. stretch. coinciding ?), 1465 and 1443 (C-H def.), 1420 ($>\text{N}-\text{C}=\text{C}-\text{NO}_2$?), 1368 (C-H def.); 1310 , 1275 , 1257 , 1240 (all strong absorptions, tentatively assigned to $>\text{N}-\text{C}=\text{C}-\text{NO}_2$), 1182 , 1152 , 1112 , 944 , 857 , 763 , 724 , 690 .

UV (n-hexane) : λ_{max} 228.5 nm (3.92), 366 (3.78).

Benzamide derivate^[224] (49), m. p. $98-99^\circ$ (ether), yield ca. 25%.

Analysis calc. for $\text{C}_{18}\text{H}_{28}\text{ON}_2$:

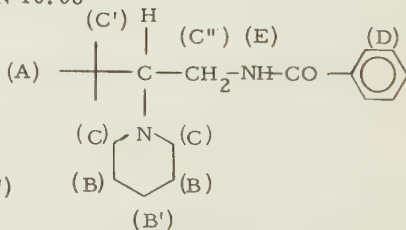
C 74.95, H 9.79, N 9.71

found C 74.79, H 10.00, N 10.08

m.w. calc. 288.4, found 273 (CH_3OH).

NMR ($\text{CDCl}_3 + \text{CF}_3\text{COOD}$) :

$\delta = 1.20$ ppm (9H, s, A),
 1.5 - 2.3 (6H, broad, B, B')
 3.15 - 4.35 (7H, m; C, C',
 C''), 7.2 - 7.9 (5H,
 m, D), 12.3 (1H, sharp, exchanged -NH-).



IR (KBr disc) : 3280 (N-H stretch.), 2930 and 2860 (C-H stretch.), 1627 (amide I), 1576 (aromat.), 1550 (amide II), 1485, 1440, 1385 and 1358 (C-H def.), 1314; 748 and 692 (C-H out-of plane of 5 adj. H).

2-Tert-butyl-2-diethylamino-1-nitroethylene (48) :

From 253.5 mg (2.0 mmoles) of tert-butyl nitroacetylene (38) in 5 ml ether with 146 mg (2.0 mmoles) of diethylamine in 5 ml ether 376 mg (94%) of (48), yellow crystals, were obtained, m. p. (Tottoli) 61-62° (from ether-petroleum ether b. p. 40-60°).

Analysis calc. for $C_{10}H_{20}N_2O_2$:

C 59.97, H 10.07, N 13.99, O 15.98

found C 59.81, H 10.12, N 14.07, O 16.27

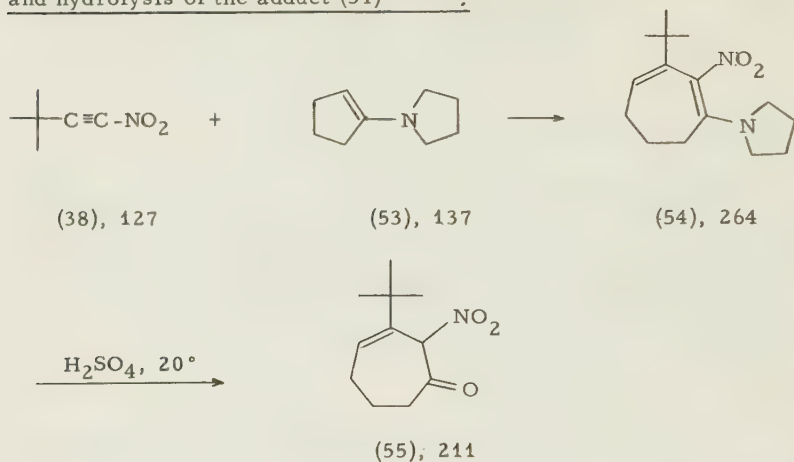
m.w. calc. 200.3, found 214 (THF).

NMR ($CDCl_3$) : δ = 1.16 ppm (6H, t, ethyl CH_3), 1.31 (9H, s, t-butyl CH_3), 3.38 (4H, q, ethyl CH_2), 6.90 (1H, s, olefinic H).

IR (KBr disc) : 3150 cm^{-1} (=C-H stretch.), sh 1565, 1540 (C=C and NO_2 asym. stretch. coinciding ?); 1456 (C-H def.), 1415 ($>N-C=C-NO_2$), 1378 and 1364 (C-H def.); 1312, 1300, 1280, 1243 (all strong bands, tentatively assigned to $>N-C=C-NO_2$), 1182, 782, 733, 719.

UV (CH_3OH) : λ_{max} 227 nm (log ϵ 3.91), 385 (4.15).

f) Reaction of tert-butyl nitroacetylene (38) with 1-pyrrolidino-cyclopentene and hydrolysis of the adduct (54) [5, 6]



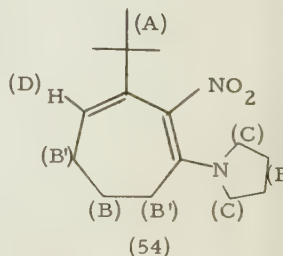
α) 3-Tert-butyl-1-pyrrolidino-2-nitro-1,3-cycloheptadiene

636.5 mg (5.0 mmoles) of tert-butyl nitroacetylene (38) in 10 ml of ether at 0° was added dropwise to 688 mg (5.0 mmoles) of the enamine^[228] (53) in 10 ml of ether. The mixture was allowed to warm up to room temperature, then the solvent was removed and the residue recrystallized from CH_2Cl_2 - petroleum ether (b.p. $40-60^\circ$) to yield 826 mg (62%) of (54), orange needles, m. p. with dec. $187-188^\circ$.

Analysis calc. for $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}_2$:

C 68.15, H 9.15, N 10.60, O 12.10
found C 68.04, H 8.99, N 10.64, O 12.08

NMR (CDCl_3) : $\delta = 1.22$ ppm (9H, s, A),
1.7-2.6 (10H, broad, B,
B' and B''), 3.1-3.7 (4H,
broad, C), 6.04 (1H,
further split triplet, D). $J_{\text{DB}'} \approx 6.5$ cps.



IR^[229] (KBr disc) : 2970 cm⁻¹ (C-H stretch.), 1615 (C=C stretch.), 1554 (>N-C=C-NO₂); sh 1480, 1465 and 1446 (C-H def.); 1408, 1275, 1255, 1231 (all strong absorptions, tentatively assigned to the >N-C=C-NO₂ system), 1162.

UV (ethanol) : $\lambda_{\max}$ sh 215 nm (log ϵ 4.05), 277.5 (3.70), 391.5 (3.99).

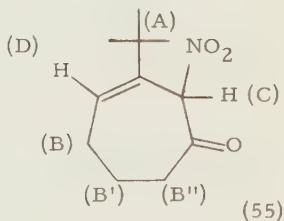
β) 3-Tert-butyl-2-nitro-3-cyclohepten-1-one (55)

267 mg (1.01 mmoles) of the nitro enamine (54) were dissolved in 3 ml of THF and 14 ml of 20% aqueous sulfuric acid added. The yellow-orange solution an standing at 30-35° slowly decolorized. One hour later the mixture had become pale yellow and colourless crystals had deposited. After addition of twice its volume of water the solution was extracted with ether, the organic layer dried over Na₂SO₄ and the solvent removed to leave a viscous oil which crystallized slowly. Recrystallization of this material provided 162 mg (76%) of (55), colourless crystals, m.p. 83-84°.

Analysis calc. for C₁₁H₁₇NO₃ :

C 62.54, H 8.11, N 6.63
found C 61.91, H 8.08, N 6.16

NMR (CDCl₃) : δ = 1.15 ppm (9H, s, A),
1.5-3.0 (6H, m, B, B' and B''), 5.65 (1H, s, c),
6.3 (1H, t, D); J_{BD} 6.0 cps.



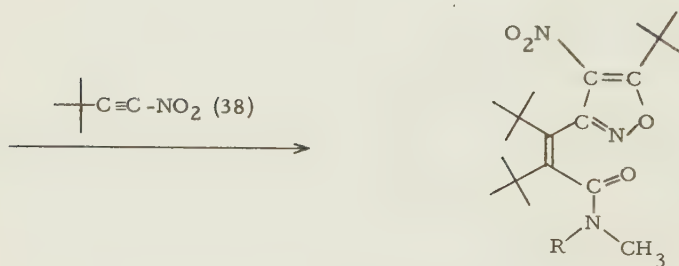
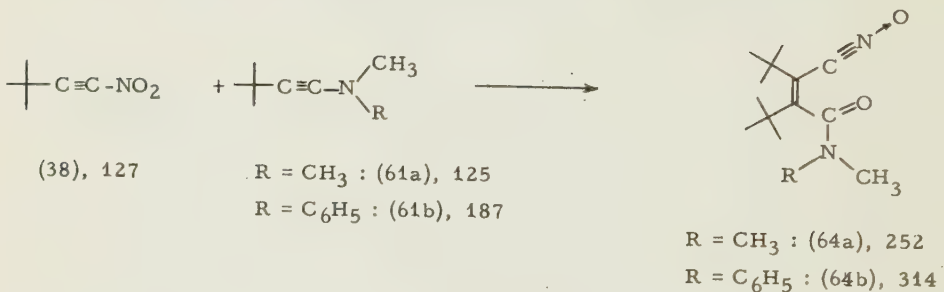
This nitro ketone did not exchange the hydrogen atom C in CF₃COOD solution within 24 hours.

[228] The supply of this enamine by Mr. A. Géronald is gratefully acknowledged.

[229] Perkin-Elmer 257 IR spectrometer.

IR (CHCl_3) : 3020 cm^{-1} (C-H stretch.), 1720 (C=O stretch.); 1562 1554 (split NO_2 asym. stretch.); 1396, 1369, 1355 and 1339 (C-H def. and NO_2 sym. stretch.), 1220, 1104, 742, 680 (in KBr).

g) Reaction of tert-butylnitroacetylene (38) with tert-butylnamines [230] (61); 1,3 dipolar additions and degradation of the 1 : 1 adducts [5, 6]



R = CH_3 : (65a), 379

R = C_6H_5 : (65b), 441

Reaction of tert-butylnitroacetylene (38) with N,N-dimethyl-tert-butylamine (61a)

a) Reactant Ratio 1 : 1; N,N-dimethyl-1,2-di-tert-butyl maleic acid nitrile oxide amide (64a)

738 mg (5.8 mmoles) of tert-butylnitroacetylene (38) in 6 ml of abs. ether were added over a period of 10 min. at 0° to a solution of 726 mg (5.8 mmoles) of N,N-dimethyl-tert-butylamine^[8](61a) in 10 ml abs. ether. After one hour at 0° the IR spectrum showed complete conversion to the nitrile oxide (64a). The solvent was drawn off and the solid material was recrystallized from ether-n-pentane to yield 429 mg (29%) of (64a), colourless needles, m.p. 82-83°. The nitrile oxide (64a) decomposed partly on recrystallization; on standing at room temperature the colourless needles changed to a pale-yellow semi-liquid mass.

Analysis calc. for C₁₄H₂₄N₂O₂, the 1 : 1 adduct (64a) :

C 66.63, H 9.59, N 11.10, O 12.68

found C 66.40, H 9.83, N 10.85, O 12.68

m.w. calc. 252.35, found 256 (benzene).

NMR (CCl₄) : δ = 1.32 and 1.42 ppm (9H each, two s, t-butyl groups),
2.98 (6H, s, N-CH₃).

IR (CCl₄) : 2280 cm⁻¹ (C≡N stretch.), 1642 (amide I), 1485 (broad),
1398 and 1368 (C-H def.), 1338 (N-O stretch.), 1272,
1172.

UV (n-hexane) : λ_{max} 261 nm (log ε 3.84).

[230] My thanks are due to Mr. M. Reinstein for providing samples of the tert-butylamines (61).

To detect thermally unstable intermediates, the reaction was run at low temperatures and followed by NMR spectroscopy. In CDCl_3 solution (nitroacetylene-ynamine ratio 1 : 2) at -60° the reaction did not occur, however, started when warmed up to -30° . No other peaks besides those of the starting compounds (38), (61a) and their 1 : 1 and 2 : 1 adducts (64a) and (65a), resp., were observed.

β) Reactant ratio 2 : 1; preparation of the 2 : 1 adduct, the isoxazole (65a)

255 mg (2.0 mmoles) of tert-butylnitroacetylene (38) were added to 128 mg (1.02 mmoles) of N,N-dimethyl-tert-butylynamine (61a) in ether at -20° and it was left standing at 0° over night. IR spectra showed only the absorptions of the 2 : 1 adduct (65a). This was isolated by removal of the solvent and crystallizing the remaining oil from petroleum ether (b. p. $40-60^\circ$). After two weeks at 0° 166 mg (44%) of (65a) had deposited as pale yellow crystals, m. p. $115-115.5^\circ$.

Analysis calc. for $\text{C}_{20}\text{H}_{33}\text{N}_3\text{O}_4$, the 2 : 1 adduct (65a) :

C 63.30, H 8.77, N 11.07, O 16.86

found C 63.54, H 8.53, N 11.02, O 17.13

m. w. calc. 379.5, found 382 (benzene).

NMR (CCl_4) : $\delta = 1.31$ and 1.34 ppm (18H, two s, t-butyl groups),
1.49 (9H, s, t-butyl), 2.50 and 2.79 (3H each, two s,
N-methyl groups).

IR (KBr disc) : 1620 cm^{-1} (amide I), 1575 (isoxazole ring), 1522 (NO_2
asym. stretch.), 1485, 1409, 1395, 1362 (NO_2 sym.
stretch.), 836.

UV (n-hexane) : no maxima, shoulders at $\lambda = 218\text{ nm}$ ($\log \epsilon = 4.06$) and
250 (3.63).

Reaction of tert-butylnitroacetylene (38) with N-methyl-N-phenyl-tert-butylamine (61b)

α) Reaction ratio $\approx 1 : 4$; preparation of the nitrile oxide (64b)

640 mg (5.04 mmoles) of tert-butylnitroacetylene (38) in 4 ml of ether were added slowly to 4.0 g (21.4 mmoles) of the ynamine^[8] (61b) in 5 ml of ether. The mixture warmed up slowly and on scratching colourless crystals started to precipitate. After 12 hours the mother liquor was sucked off and the remaining crystals washed 3 times with n-pentane at 0°. Yield of 1 : 1 adduct, the nitrile oxide (64b) 66% (1.043 g), m.p. 138°.

Analysis calc. for $C_{19}H_{26}N_2O_2$, the 1 : 1 adduct (64b) :

C 72.35, H 8.34, N 8.91, O 10.18

found C 72.54, H 8.52, N 8.91, O 10.27

m.w. calc. 314.4, found 323 ($CHCl_3$).

NMR ($CDCl_3$) : two geometric isomers in 89:11 ratio:

main isomer $\delta = 1.43$ and 1.46 ppm (18H, two s, 2 t-butyl groups),
3.32 (3H, s, $N-CH_3$);

minor isomer $\delta = 1.16$ and 1.21 ppm (18H, two s, 2 t-butyl groups),
3.39 (3H, s, $N-CH_3$);

the phenyl protons of both isomers appeared at 7.25-7.5 ppm (5H, m).

IR (KBr disc) : 2285 cm^{-1} ($C\equiv N$ stretch.), 1635 (amide I), 1598 and 1495 (aromat.), 1398 and 1370 ($C-H$ def.), 1330 ($N-O$ stretch.), 763 and 695 ($C-H$ out-of-plane def. from 5 adjacent H).

UV (in n-hexane) $\lambda_{\max}$ 241.5 nm ($\log \epsilon$ 3.93);
(in methanol) 240 (3.95), 253 (3.93).

β) Reactant ratio 1:1, isolation of 1:1 and 2:1 adducts (64b) and (65b), resp.

The reaction was carried out as described above. 1.27 g (10.0 mmoles) of tert-butyl nitroacetylene and 1.87 g (10.0 mmoles) of the tert-butyl-ynamine yielded 660 mg (21%) of the nitrile oxide (64b) that crystallized from the solution. The mother liquor was evaporated and diluted with its volume of n-pentane. After several days at room temperature 900 mg (41%) of the colourless 2:1 adduct (65b) had crystallized, m.p. 131-132°. Total yield based on the nitroacetylene (38) 62%.

Analysis calc. for $C_{25}H_{35}N_3O_4$, the 2:1 adduct (65b) :

C 68.00, H 7.99, N 9.52, O 14.49

found C 67.84, H 8.07, N 9.65, O 14.49

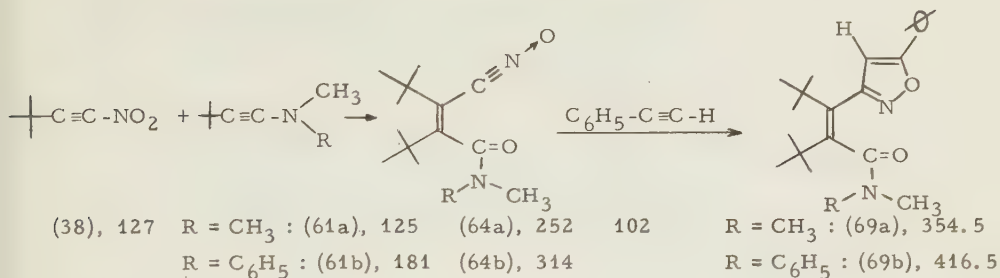
m.w. calc. 441.55, found 452 (THF).

NMR ($CDCl_3$) : δ = 1.37, 1.40 and 1.48 ppm (27H, 3 s, three t-butyl groups), 3.22 (3H, s, N-CH₃), 6.8 - 7.4 (5H, m, phenyl H).

IR (CCl_4) : 1655 cm^{-1} (amide I), 1602 (aromat.), 1585 (isoxazole), 1533 (NO_2 asym. stretch.), 1503 (aromat.), 1487, 1435, 1410, 1400, 1366 (NO_2 sym. stretch), 1208, 1158, 1110, 834, 695 (5 adj. H).

UV (n-hexane) : λ_{max} 234 nm (log ϵ 4.11).

Reaction of the 1:1 adducts, the nitrile oxides (61), with phenylacetylene (68)



α) N,N-Dimethyl 1,2-di-tert-butyl-2-(3-phenylisoxazol-5-yl)-acrylamide (69a)

256 mg (2.01 mmoles) of tert-butylnitroacetylene (38) were added at 0° over a period of 30 min. to a solution of 252 mg (2.01 mmoles) of N,N-dimethyl tert-butylnamine (61a) in 2.5 g (24.5 mmoles) of phenylacetylene (68). After four hours at room temperature the nitrile oxide triple bond absorption of (64a) in the IR had almost completely vanished and the solvent was then drawn off. The remaining oil was separated by LSC on silicagel (ethyl acetate-cyclohexane 30:70) and provided 346 mg (69%) of the isoxazole derivative (69a), a slightly yellow oil.

Analysis calc. for C₂₂H₃₀N₂O₂ :

C 74.25, H 8.78, N 7.49, O 9.62

found C 74.12, H 9.05, N 7.86, O 8.68

m.w. calc. 354.5, found 318 (THF).

NMR (CCl₄) : δ = 1.30 and 1.37 ppm (18H, two s, 2 t-butyl groups),
 2.42 and 2.75 (6H, two s, N-CH₃), 6.36 (1H, s,
 olefinic H), 7.3 - 7.9 (5H, m, phenyl H).

IR (film) : sh 3080 cm^{-1} ($=\text{C}-\text{H}$ stretch.), 1626 (amide I), 1595 (aromat.), 1575 (isoxazole), 1492 and 1450 (aromatic), 1388 (isoxazole), 1360 ($\text{C}-\text{H}$ def.), 764 and 690 ($\text{C}-\text{H}$ out-of-plane def. of 5 adj. H).

UV (cyclohexane) : λ_{max} sh 213.5 nm (4.29), 265 (4.32).

β) N-Methyl-N-phenyl 1,2-di-tert-butyl-2-(3-phenyl-isoxazol-5-yl) acryl-
amide (69b)

128 mg (0.41 mmole) of the N-phenyl-N-methyl nitrile oxide amide (64b) were dissolved in 1.0 g (10 mmoles) of phenylacetylene (68). After two days at room temperature most of the excess phenylacetylene was removed under high vacuum. The remaining product was crystallized from ether - petroleum ether (b. p. $40-60^\circ$) and washed 4 times with n-pentane. Yield of the isoxazole (69b) 117 mg (69%), m. p. 130° .

Analysis calc. for $\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_2$:

C 77.85, H 7.74, N 6.73, O 7.68

found C 77.81, H 7.86, N 6.81, O 8.07

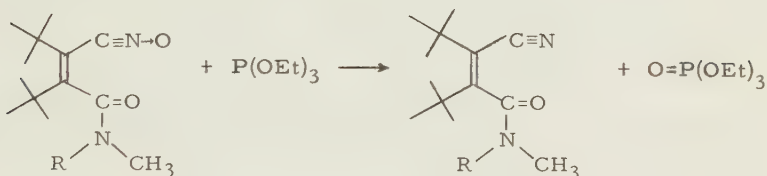
m.w. calc. 416.5, found 410 (THF).

NMR (CDCl_3) : 1.35 and 1.52 ppm (18H, two s, two t-butyl groups), 3.24 (3H, s, $\text{N}-\text{CH}_3$), 6.50 (1H, s, olefinic H), 6.65 - 7.25 (5H, m, N-phenyl H), 7.3 - 7.9 (5H, m, phenyl H of the isoxazole substituent).

IR (KBr disc) : sh 3020 cm^{-1} ($=\text{C}-\text{H}$ stretch.), 1630 (amide I), 1597 (aromat.), 1575 (isoxazole), 1496 and 1453 (aromat), 1380 (isoxazole), sh 1366; 762, 695 and 687 ($\text{C}-\text{H}$ out-of-plane def. for 5 adj. H; from two different phenyl groups).

UV (methanol) : $\lambda_{\max}$ 263 nm (4.38).

Reduction of nitrile oxides by triethyl phosphite^[50]



R = CH₃ : (64a), 252 166

R = CH₃ : (66a), 234

R = C₆H₅ : (64b), 314

R = C₆H₅ : (66b), 298

α) Preparation of the N,N-dimethyl amide nitrile (66a)

252 mg (1.0 mmole) of the nitrile oxide (64a) from tert-butyl nitroacetylene (38) and N,N-dimethyl-tert-butylamine (61a) were dissolved in 10 ml of dry benzene and a fourfold excess of triethyl phosphite (665 mg = 4.0 mmoles) was added. After 15-20 min. of heating on the water bath the mixture was diluted by its volume of benzene and shaken with 20 ml of 5% aqueous H₂SO₄ to destroy excess phosphite. When the characteristic odour of (EtO)₃P had disappeared, the organic layer was washed (4 times) with water and then evaporated. The remaining oil was recrystallized from n-pentane at 0° to yield 201 mg (85%) of (66a), forming long, colourless needles, m.p. 87-87.5°.

Analysis calc. for C₁₄H₂₄N₂O :

C 71.14, H 10.24, N 11.85, O 6.77

found C 71.09, H 10.12, N 12.04, O 7.21

m.w. calc. 236.35, found 236 (benzene).

NMR (CCl_4) : $\delta = 1.33$ and 1.42 ppm (18H, two s, two t-butyl groups),
2.92 and 2.95 (6H, two s, N-CH_3).

Neither addition of iodine nor heating up to 95° for one week gave any isomerization of (66a) as found with the corresponding N-methyl-N-phenyl derivative (66b) (see below).

IR (KBr disc) : 2230 cm^{-1} ($\text{C}\equiv\text{N}$ stretch.), 1630 (amide I), 1496, 1469, 1408, 1394, 1368 (C-H def.), 1209, 1172, 1102, 989, 655.

UV (n-hexane) : λ_{max} 205.5 nm ($\log \epsilon$ 4.17), 241 (3.51).

β) Preparation of the N-methyl-N-phenyl amide nitrile (66b)

The corresponding nitrile oxide (64b) derived from N-methyl-N-phenyl tert-butyldynamine (61b) was reduced to the nitrile (66b) analogously. 206 mg (0.655 mmole) of the nitrile oxide (64b) afforded 177 mg (90%) of the nitrile (66b), m.p. 146° .

Analysis calc. for $\text{C}_{19}\text{H}_{26}\text{N}_2\text{O}$:

C 76.47, H 8.78, N 9.39, O 5.36

found C 76.42, H 8.71, N 9.05, O 5.89

m.w. calc. 298.4, found 280 (THF).

NMR : in CDCl_3 solution the isolated nitrile (66b) slowly isomerized. After 10 days at room temperature the final ratio 56:44 was established;

starting isomer $\delta = 1.46$ ppm (18H, s, two coinciding t-butyl groups),
3.35 (3H, s, N-CH_3);

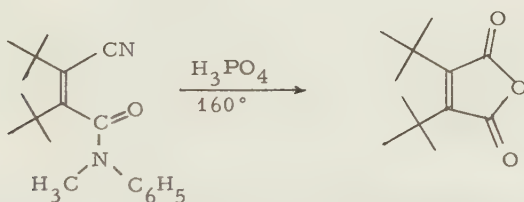
new isomer 1.16 and 1.25 ppm (18H, two s, 2 t-butyl), 3.38 (3H, s, N-CH_3);

phenylprotons undistinguishable multiplet 7.25-7.5 ppm.

IR (KBr disc) : 2205 cm^{-1} ($\text{C}\equiv\text{N}$ stretch.), 1635 (amide I), 1595 and 1495 (aromat.), 1470, 1370, 1208, 766 and 696 (C-H def. 5 adj. H), 730.

UV (methanol) : λ_{max} 204.5 nm ($\log \epsilon$ 4.34), sh 220 (4.1), sh 240 (3.92).

Hydrolysis of N-methyl-N-phenyl 1,2-di-tert-butylmaleic acid nitrile amide (66b) to di-tert-butyl maleic acid anhydride



(66b), 298

(67), 210

190 mg (0.637 mmole) of the nitrile amide (66b) were heated for 20 hours with 5 ml of 85% H_3PO_4 . After cooling the mixture was dissolved in saturated NaHCO_3 solution - ether. The aqueous phase contained no organic material. From the organic layer by removal of the solvent and recrystallization (ether/n-pentane) 130 mg (97%) of the anhydride (67) were obtained; colourless crystals, m.p. $88.5 - 89.5^\circ$ (Tottoli).

Analysis calc. for $\text{C}_{12}\text{H}_{18}\text{O}_3$:

C 68.54, H 8.63, O 22.83

found C 68.04, H 8.60, O 23.08

m.w. calc. 210.3, found 237 (benzene).

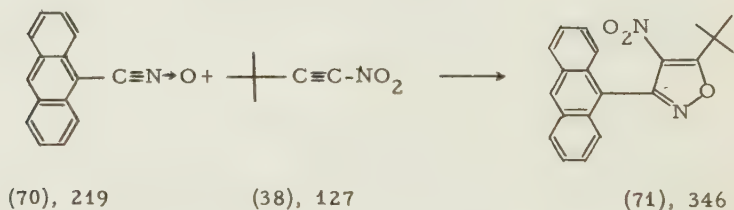
NMR (CCl_4) : one peak at $\delta = 1.49$ ppm.

IR (KBr disc) : 2970 cm^{-1} (C-H stretch.), 1830 and 1755 (C=O stretch.), 1627 (weak abs. band, C=C stretch. ?); 1488, 1465, 1401 and 1371 (C-H def.), 1260 (C-O stretch.), 952, 756, 726.

UV (n-hexane) : λ_{max} 209 nm (log ϵ 3.90), 251.5 (3.79).

Mass spectrum : m/e 210 $[\text{M}]^+$, 195, 192, 182, 177, 167, 166, 164, 154, 151, 149, 139, 127, 126, 123, 111, 110, 109, 95, 93, 91, 81, 77, 67, 65, 57, 53, 51, 44, 41 (base peak).

h) Reaction of tert-butylnitroacetylene (38) with anthracyl-9-fulmide (70)^[5, 6]



9-Anthracyl-fulmide (71) was prepared by converting anthracene-9-aldehyde^[231] into its oxime^[232] and subsequent dehydrogenation by NaOH/ Br_2 ^[196]. Care had to be taken especially in the synthesis of the syn-oxime. Only the syn, not the anti isomer can be oxidized to the nitrile oxide^[232].

137 mg (1.08 mmole) of tert-butylnitroacetylene (38) and 219 mg (1.00 mmole) of the nitrile oxide (71) were dissolved in 10 ml of benzene. After 4 hours at room temperature the solvent was distilled off and the remaining solid recrystallized from CH_2Cl_2 -petroleum ether (b.p. 60-80°).

Yield 322 mg (93%) of the isoxazole (71), yellow crystals, m.p. 179-181° with dec. (Tottoli).

Analysis calc. for $C_{21}H_{18}N_2O_3$:

C 72.82, H 5.24, N 8.09, O 13.86

found C 72.55, H 5.27, N 8.25, O 14.08

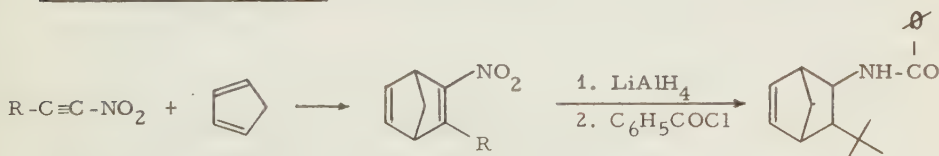
m.w. calc. 346.4, found 352 (benzene).

NMR ($CDCl_3$) : δ = 1.61 ppm (9H, s, t-butyl group), 7.3 - 8.2 (8H, m, protons of the outer rings), 8.57 (1H, s, H in 10-position).

IR (KBr disc) : 1628 cm^{-1} (aromat.), 1585 (isoxazole), 1518 and 1368 (NO_2 asym. and sym. stretch.), 1130 and 1015 (isoxazole), 895 (C-H out-of-plane def. of one free H), 834, 788, 738 (C-H def. of 4 adjacent H).

UV ($CHCl_3$) : λ_{max} 256.5 nm (log ϵ 5.12), sh 320 (3.22), 335 (3.53), 350 (3.78), 367.5 (3.90), 388 (3.82).

i) Reaction of tert-butyl and iso-propylnitroacetylene (38) and (39), resp., with cyclopentadiene^[1,5]



R = t-Bu : (38), 127 (72), 66 (74), 193 (78), 269

R = i-Pr : (39), 113 (75), 179

[231] E. Campaigne and W.L. Archer, J. Amer. chem. Soc. 75, 989 (1953).

[232] a) L.F. Fieser and J.L. Hartwell, *ibid.* 60, 2555 (1938);

b) J.S. Meek and J.R. Dann, *ibid.* 77, 6677 (1955).

Cf. also *loc. cit.* [119a].

α) 2-tert-Butyl-3-nitro-norbornadiene (74)

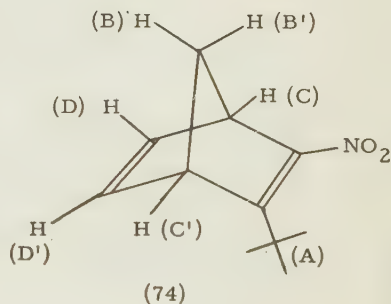
To 0.92 g (7.25 mmole) of the nitroacetylene (38) 3.5 ml of cyclopentadiene [233] were added. After 14 hours excess diene was drawn off. The residue was separated by LSC on silicagel. Cyclohexane eluted the dicyclopentadiene (73), then with benzene a slightly yellow solution of the norbornadiene derivative (74) was collected. The solvent was removed in vacuo leaving a yellow oil which by bulb tube distillation yielded 1.24 g (89%) of the yellow liquid diene adduct (74), b. p. 60-62°/0.15 mm. GLC : peak at 168°.

Analysis calc. for $C_{11}H_{15}NO_2$:

C 68.37, H 7.82, N 7.25

found C 68.53, H 7.77, N 6.96

NMR (CCl_4) : δ = 1.15 ppm (9H, s, A),
2.07 (2H, split quartet,
B and B'), 3.8 (2H, m,
tertiary protons C and
C'), 6.7 - 7.2 (2H, split
doublets D and D'). $J_{BB'}$
6.5 cps, $J_{DD'}$ 5 cps.



IR (film) : 2970 cm^{-1} and 2880 (C-H stretch.), 1590 broad (C=C stretch. with NO_2 subst.), 1558 (C=C stretch.), 1506 (NO_2 asym. stretch.); 1482, 1465, and 1397 (C-H def.), 1351 (NO_2 sym. stretch.), 1300, 1255, 837, 827, 790, 768, 720 (C-N vibr.).

UV (n-hexane) : λ_{max} sh 225 nm (log ϵ 3.49), sh 250 (3.44), 291.5 (3.18).

[233] Freshly prepared by the pyrolysis of dicyclopentadiene (Schuchardt).

β) Benzamid derivative (78)^[224]

Colourless needles, m.p. 148-150°, b.p. ≈ 140°/0.1 mm.

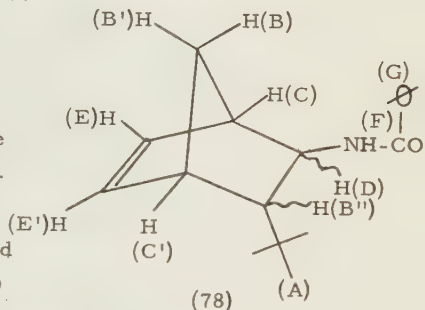
Analysis calc. for $C_{18}H_{23}NO$:

C 80.25, H 8.61, N 5.20

found C 80.08, H 8.68, N 4.99

m.w. calc. 269.4, found 238 (methanol).

NMR (CCl_4) : 0.88 ppm (9H, s, A)
 1.6 (3H, broad; bridge protons B, B' and tertiary proton B''), 2.8 (2H, broad, bridgehead protons C and C'), 3.9 (0.8H, very broad multiplet, D), 6.11 (2H, "triplet", E and E'), ≈ 6.5 (0.7H, broadened, NH proton F), 7.25 - 7.8 (5H, m, G).



IR (KBr disc) : 1615 cm^{-1} (amide I), 1578 (aromat. or C=C stretch.), 1456 (aromat.), 1398 and 1370 (C-H def.), 1357, 752 and 692 (C-H def. of 5 adj. H), 710.

γ) 2-iso-propyl-3-nitro-norbornadiene (75)

From 490 mg (4.34 mmoles) of the nitroacetylene (39) and excess cyclopentadiene after LSC 36.8 mg (47%) of yellow crystals were obtained, m.p. 33-35° (Tottoli). Further purification (distillation and recrystallization from n-pentane at -20°) afforded crystals melting at 36.5-37° (Tottoli). GLC : 172°. This compound (75) decomposed on standing at room temperature.

Analysis calc. for $C_{10}H_{13}NO_2$:

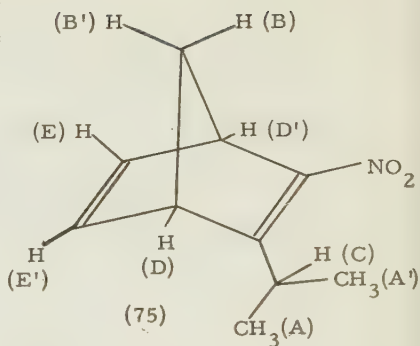
C 67.02, H 7.31, N 7.82

found C 66.51, H 6.82, N 7.74

NMR (CCl_4) :

δ = 0.94 and 1.26 ppm

(6H, two doublets, A and A'), 2.12 (2H, "triplet", B, B'), 3.35-4.1 (3H, two multiplets from D and D' superimposed by the multiplet of C), 6.88 (2H, split doublets, E and E').



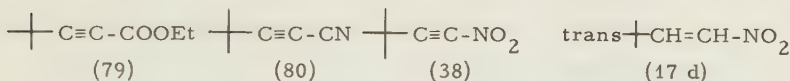
IR (film) :

3080 cm^{-1} weak sh (=C-H stretch.), 2980 and 1890, (C-H stretch.), 1619 (C=C stretch. with NO_2 subst.), 1562 (C=C stretch.), 1500 (NO_2 asym. stretch); 1468, 1390 (C-H def.), 1351 (NO_2 sym. stretch.), 1321, 1302, 1233, 1210, 1029, 1007, 812, 774, 760, 724 (C-N vibr.), 674.

UV (n-hexane) :

λ_{max} sh 225 nm (3.57), 247.5 (3.71), 296 (3.57).

Comparison of the Dienophilic Activity of tert-Butylnitroacetylene with other tert-Butylacetylenes and tert-Butylnitroethylene towards Cyclopentadiene.



Ethyl tert-butylacetylene carboxylate (79) was prepared from tert-butylacetylene as follows: tert-butylacetylene^[220] was converted to the corresponding carboxylic acid via its Grignard compound and then esterified^[234]. Aminolysis of this ester afforded the corresponding amide which was dehydrated with P₂O₅ to the nitrile^[235]. For the preparation of t-butylnitroethylene, see p. 172.

1 mmole of each of these four dienophiles was mixed with 1 ml of cyclopentadiene and the reaction followed by GLC analyses. The nitroacetylene had completely reacted after $\approx$ 1.5 hours at room temperature, whereas analyses of the other samples after several days showed no formation of adducts.

[234] Cp. a) Moureau and Delange, C.R. hebd. Séances Acad. Sci. 136, 553 (1903) ;

b) Org. Syntheses, Coll. Vol. I, 524 (1932) ;

c) R. Fuks, ERA Brussels, personal communication.

[235] B. Fischer and C.A. Grob, Helv. Chim. Acta 39, 417 (1956).

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Configurational assignment of trisubstituted olefins :
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Lebenslauf

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